VOL. XLIV. AUGUST, 1910. NO. 2.

AMERICAN CHEMICAL JOURNAL

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXI.—ALKYLATION OF AROMATIC AMINO ACIDS: AMINOMETHYLBENZOIC ACIDS.

[THIRD PAPER.]

BY HENRY L. WHEELER AND CHARLES HOFFMAN.

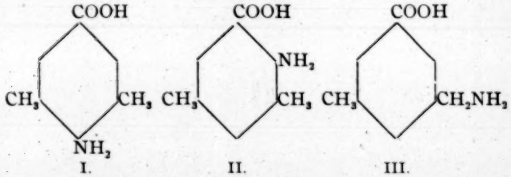
A review of the literature on the alkylation of aminobenzoic acids by means of alkali and alkyl halides was given in a recent article.[1] It was shown that while *o*-, *m*-, and *p*-aminobenzoic acids give N-alkylamino acids, certain substituted aminobenzoic acids, on the other hand, give esters. The amino acids having negative groups adjacent to the amino radical, as, for example, 3,5-diiod-*o*-aminobenzoic acid, 3,5-diiod-*p*-aminobenzoic acid, 3,5-dinitro-*p*-aminobenzoic acid, and 3-nitro-*o*-aminobenzoic acid, give esters; while 4-nitro-*o*-aminobenzoic acid, isomeric with the latter acid, but not having substituents in both of the adjacent positions to the amino group, gives N-alkyl derivatives.

With these results at hand, it was of interest to determine whether or not a similar protecting influence from substitution in the amino group is exerted by substituents which are not generally considered as having a negative character—the methyl group, for example. This also has the smallest molecular weight.

For this purpose the following aminomesitylenic acids were

[1] THIS JOURNAL, **43**, 398 (1910).

selected: 3,5-dimethyl-*p*-aminobenzoic acid (I) and 3,5-dimethyl-*o*-aminobenzoic acid (II).[1]

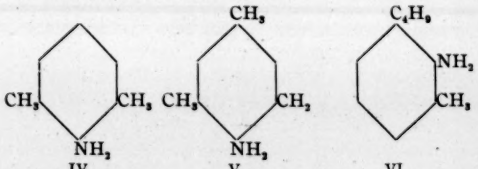


I. II. III.

It must be remembered that in the alkylations we are dealing with the potassium salts of the acids in alcoholic solution and not the free acids. The alkali neutralizes the negative effect of the carboxyl group and therefore increases the positive character of the molecule.

It is interesting, in this connection, therefore, to note the behavior of similar amines. Friedlander[2] has shown that vicinal *m*-xylidine (IV) gives N-mono- and dialkyl derivatives with alkali and alkyl halides, less readily than aniline, while Fischer and Windaus[3] showed that this base does not give a quaternary ammonium iodide.

Mesidine (V) gives a secondary and a tertiary base but not a quaternary salt,[4] while Effront discovered that isobutyltoluidine (VI) was not alkylated at all by potassium hydroxide and methyl iodide, even at 140°.[5]



IV. V. VI.

[1] It is a noteworthy property of both the above amino-3,5-dimethylbenzoic acids that the hydrochlorides are hydrolyzed by water; when crystallized from water, the free acids are obtained and not the salts. This negative influence of the methyl groups was first observed in the case of 4-amino-3,5-dimethylbenzoic acid by Fittig and Brückner (Ann. Chem. (Liebig), **147**, 50).

[2] Monats. Chem., **19**, 644 (1898).

[3] Ber. d. chem. Ges., **33**, 345.

[4] Hofmann: Ber. d. chem. Ges., **5**, 718. Fischer and Windaus: *Loc. cit.*

[5] Ber. d. chem. Ges., **17**, 2346.

We have found that when 3,5-dimethyl-4-aminobenzoic acid (I) was warmed in alcohol with four molecular proportions of potassium hydroxide and five of ethyl iodide the alkylation took place slowly and the only product obtained besides unaltered acid was a primary amino ester,

$$(CH_3)_2C_6H_2(NH_2)COOC_2H_5.$$

In this case two methyl groups in the ortho position prevent the alkylation of the amino group.

When the isomeric acid, 3,5-dimethyl-2-aminobenzoic acid, was treated with potassium hydroxide and ethyl iodide, under the same conditions, a striking difference in behavior was observed. The acid underwent alkylation easily in a short time and the product consisted almost entirely of the N-diethylamino acid (30)[1] and the monoethylamino acid (10). A small amount of the ester (1) and unaltered acid (5) was also obtained.

In view of the behavior of the isomeric acid this seems to be a very curious result. In this case a methyl and a —COOK group in the ortho positions do not prevent the alkylation of the amino group. In fact they favor it, although the —COOK group has a much greater molecular weight than methyl. Here the stereochemical interference that might be expected is not shown in the reaction.

This result would be best explained if this amino acid had the structure represented by formula (III), but the statements of Jacobsen that with nitrous acid the acid gives oxymesitylenic acid and then 1,3,4-metaxylenol,[2] and the observations of Schmitz,[3] who obtained the corresponding *m*-xylidine, are against this view. We have found that the ester of the nitro acid, from which the amino acid was prepared, does not have the properties of a compound containing the group $—CH_2NO_2$. It is insoluble in alkali. Formula (III) is therefore excluded.

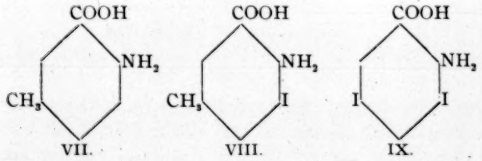
We have also examined the behavior on alkylation of methylanthranilic acid, 2-amino-5-methylbenzoic acid (VII), and

[1] The numbers in parentheses represent the relative parts by weight of the substances obtained.

[2] Ber. d. chem. Ges., **11**, 2055 (1878).

[3] Ann. Chem. (Liebig), **198**, 160.

of 2-amino-3-iod-5-methylbenzoic acid (VIII). The structure of the latter acid has not been settled, but from the behavior of anthranilic acid on iodation[1] it undoubtedly contains the iodine in the 3 position.



VII. VIII. IX.

2-Amino-5-methylbenzoic acid alkylated readily and in a normal manner under the above conditions, giving a N-monoethylamino acid (15 parts) as the chief product. There were formed some N-diethylamino acid (1 part) and a small amount of material insoluble in ammonia (2 parts). This was probably the ester $CH_3C_6H_3(NH_2)COOC_2H_5$.

2-Amino-3-iod-5-methylbenzoic acid, prepared by treating methylanthranilic acid with iodine monochloride, alkylates with difficulty. The chief product besides unaltered acid (30 parts) was found to be the primary amino ester

$$CH_3C_6H_2I(NH_2)COOC_2H_5$$

(15 parts). A small quantity of the N-diethylamino acid (4 parts) was also obtained.

A —COOK group and an iodine atom in the ortho position to an amino group therefore exert an interference on the alkylation of the amino group. This interference is more pronounced when iodine also occupies the para position to the amino group than when methyl is present in this position. 3,5-Diiod-2-aminobenzoic acid (IX) gives no N-alkyl derivative, and no addition to or an alkylation on the nitrogen was observed when the ester of this acid was dissolved in ethyl iodide and the solution allowed to stand.[2]

These results show that neither the theory of stereochemical interference nor the positive or negative character of the

[1] Wheeler and Johns: THIS JOURNAL, **43**, 398 (1910).
[2] THIS JOURNAL, **43**, 409 (1910).

substituents is sufficient to give an explanation of the different behavior of amino acids on alkylation, and that other influences are at work to determine the course of the reaction. This subject will receive further attention when more data are collected.

The aminomethylbenzoic acids were obtained by reducing the corresponding nitro acids. 2-Nitro-5-methylbenzoic acid was prepared by nitrating *m*-toluic acid. Jacobsen[1] stated that 2-nitro-3-methylbenzoic acid and 2-nitro-5-methylbenzoic acid are formed in this nitration, the former in much larger amount.

This statement is incorrect. Panaotovic[2] showed that the chief product of the nitration is 2-nitro-5-methylbenzoic acid, melting at 219°, and we have now found that the isomeric acid which also results in this reaction is 4-nitro-3-methylbenzoic acid, melting at 211°, and not 2-nitro-3-methylbenzoic acid. The latter acid has not yet been prepared. We have found that the material supposed by Jacobsen to be this acid, melting at 182°, is a mixture of the acids melting at 219° and 211°. This material and the amino product obtained by reduction should be stricken from the list of acids.

EXPERIMENTAL PART.

3,5-Dimethylbenzoic acid (*mesitylenic acid*) was prepared by oxidizing mesitylene with dilute nitric acid. This is Fittig's method,[3] but he does not give the yields. Our experience with the method was as follows: Fifty-three grams of mesitylene were warmed on the steam bath with about 190 cc. of concentrated nitric acid diluted with two volumes of water; after being warmed about 40 hours under a return condenser, the oil was completely converted into a colorless crystalline mass. The acid solution and the crystalline material were separately distilled in steam. On adding alkali to the distillates, concentrating and precipitating with hydrochloric acid, 22.5 grams of mesitylenic acid, melting at 165°–166°, were obtained.

[1] Ber. d. chem. Ges., **14**, 2353 (1881).
[2] J. prakt. Chem., [2] **33**, 63 (1886).
[3] Ann. Chem. (Liebig), **141**, 144 (1867)

The residue from the crystalline material that did not distil in steam was converted into barium salts and the first crop of crystals which separated was recrystallized from water. On decomposing the salt then with hydrochloric acid, 1.5 grams of 4-nitro-3,5-dimethylbenzoic acid, melting at 212°–217°, were obtained.

The first filtrate from the barium salts was acidified with hydrochloric acid; this gave 23 grams of a mixture of acids melting at 270°–300°. Uvitic acid melts at 287° and trimesic acid above 300°.

The filtrate from the recrystallized barium salts, on acidifying with hydrochloric acid, gave a mixture of 4-nitro-3,5-dimethylbenzoic acid and uvitic acid. This was reduced with ferrous sulphate and ammonia, and on filtering, concentrating and acidifying with hydrochloric acid 4 grams of uvitic acid, melting at 274°,[1] were obtained. On making the solution alkaline with ammonia, then precipitating with acetic acid, we obtained 1.4 grams of *4-amino-3,5-dimethylbenzoic acid*.

In the above experiment a considerable quantity of the mesitylene was converted into high melting acids. This suggests that if a weaker nitric acid, or a smaller amount of it, were employed, or if the mixture were not warmed so long, a better yield of mesitylenic acid would result.

2- and 4-Nitro-3,5-dimethylbenzoic Acids.—The mesitylenic acid obtained above was nitrated according to Bamberger's directions.[2] In regard to the yields of the two acids formed there is only the statement of Schmitz[3] that the β acid or 4-nitro-3,5-dimethylbenzoic acid results in relatively small amount.

We have obtained, by nitrating 22.5 grams of mesitylenic acid, 19.5 grams of 2-nitro-3,5-dimethylbenzoic acid and less than one gram of the 4-nitro acid. In one experiment 20 grams of mesitylenic acid gave 25 grams of the mixed nitro acids.

The acids (23 grams) were separated as follows: The mix-

[1] Fittig and Furtenbach: Ann. Chem. (Liebig), **147**, 295.
[2] Ber. d. chem. Ges., **34**, 27 (1901).
[3] Ann. Chem. (Liebig), **193**, 168 (1878).

ture was converted into the barium salts and the more difficultly soluble portion containing the 4-nitro-3,5-dimethylbenzoic acid was removed. On acidifying the filtrate the 2-nitro acid separated (19.5 grams).

The product precipitated (3.5 grams) from the barium salts that were removed melted at 174°–176°; this agrees with the melting point of 4-nitro-3,5-dimethylbenzoic acid given by Schmitz. On crystallizing the sample once from alcohol the melting point rose to 190°–217°. The mixture was reduced, and in one experiment, on crystallizing the resulting amino acids, the two isomers were obtained, one melting at 190°, the other at 242°; in the present case the amino acids (2 grams) were alkylated as described below, but only 0.24 gram of 4-amino-3,5-dimethylbenzoic acid was obtained, along with a small amount of the ester.

When the sample of 4-nitromesitylenic acid, obtained by oxidizing mesitylene with nitric acid, and melting at 212°–217°, was recrystallized from water it melted at 215°–218°. There was therefore no such lowering of melting point on crystallizing from water as described by Jacobsen.[1] In this respect our observation agrees with that of Emerson[2] on this acid.

2- and 4-Amino-3,5-dimethylbenzoic Acids.—The nitro acids were reduced with ferrous sulphate and ammonia, ten molecular proportions of the crystallized iron salt and 2 cc. of concentrated ammonia per gram of acid being used. This method of reduction gave a much better yield than tin and hydrochloric acid. One and a half grams of 4-nitro-3,5-dimethylbenzoic acid gave 1.1 grams of the amino acid; and 19.5 grams of the 2-nitro acid gave 14 grams of 2-amino-3,5-dimethylbenzoic acid.

From 53 grams of mesitylene we obtained 14 grams of 2-amino-3,5-dimethylbenzoic acid melting at 190°, and 2.74 grams of 4-amino-3,5-dimethylbenzoic acid, melting at 242°. Fittig[3] gives 235° and Emerson[4] 245°.

[1] Ber. d. chem. Ges., **11**, 2054.
[2] This Journal, **8**, 269 (1886).
[3] Ann. Chem. (Liebig), **147**, 50.
[4] *Loc. cit.*

Method of Alkylation and Separation of the Products.—The alkylations described in this paper were carried out as nearly as possible in the same manner. The amino acids were dissolved in absolute alcohol containing four molecular proportions of potassium hydroxide, and five molecular proportions of ethyl iodide were added. The solutions were heated on the steam bath for 2–6 hours. If they developed an acid reaction the heating was stopped. The alcohol was then evaporated and the dry residue was treated with a little water. This dissolved any unaltered potassium salt, and since the acids are very difficultly soluble in cold water they could be precipitated by means of acetic acid. This gave an idea of the completeness of the reaction. The material left undissolved by water was then treated with cold, dilute ammonia, three parts of water to one of concentrated ammonia; after this treatment the residue, in each case, consisted of the primary amino ester. On adding acetic acid to the filtered ammonia solution any unaltered acid set free in the reaction was recovered. The N-alkyl acids, being soluble in water, were obtained on evaporating the solutions, acidified with acetic acid, to dryness and extracting the residues with organic solvents, ethyl acetate, etc. The N-dialkyl acids were separated from the other acids in this extract by taking advantage of their solubility in petroleum ether.

Ethylation of 3,5-Dimethyl-4-aminobenzoic Acid.

Ethyl 3,5-Dimethyl-4-aminobenzoate.—One and two-tenths grams of the 4-amino acid and ethyl iodide and potassium hydroxide, in the proportions stated above, were heated in 30 cc. of absolute alcohol for five hours on the steam bath in a flask attached to a return condenser. The alcohol was then evaporated and the residue treated with water. From the aqueous solution acetic acid precipitated 0.75 gram, or 62 per cent. of the original amount, of unaltered acid, melting at 242°. When mixed with a sample of the original acid the melting point was not lowered. The reaction therefore was not complete.

The residue was treated with dilute ammonia; it did not

dissolve, and, on drying, weighed 0.6 gram, or 42 per cent. of the calculated.

This ester is readily soluble in benzene and alcohol, difficultly soluble in hot water, and moderately soluble in petroleum ether, from which it crystallizes in beautiful, colorless plates, melting to a clear oil at 67°.

	Calculated for $C_{11}H_{15}O_2N$.	Found.
N	7.25	7.28

When this substance was boiled with potassium hydroxide and the solution was acidified with acetic acid, 4-amino-3,5-dimethylbenzoic acid, melting at 242°, was obtained.

The above alkylation was repeated with two molecular proportions of potassium hydroxide and six of ethyl iodide and the mixture was digested on the steam bath for five days. Instead of increasing the yield of ester, this treatment caused decomposition, the products being a tar containing iodine and a small amount of unaltered acid.

Ethylation of 3,5-Dimethyl-2-aminobenzoic Acid.

3,5-Dimethyl-2-diethylaminobenzoic Acid.—Six grams of the acid were treated as above for 4 hours. The residue, on evaporation, almost all dissolved in water; an oily substance remained which, after treating with dilute ammonia and drying over sulphuric acid, weighed 0.1 gram. The amount of this was too small for purification, but it was shown to be the primary amino ester by saponification with alkali and precipitation with acetic acid, the regenerated acid melting at 190° being obtained. The ammonia solution, on acidifying with acetic acid, gave 0.5 gram of unaltered acid, and on evaporation only a very small residue remained.

The aqueous solution above gave no precipitate with acetic acid. It was evaporated to dryness and repeatedly extracted with ethyl acetate. The ethyl acetate extract was then extracted with petroleum ether; a part, which proved to be the N-monoethyl acid, remained undissolved. From the petroleum ether solution clear, colorless, prismatic crystals, melting to an oil at 98°, separated. About three grams of this

material were obtained. The following analyses show that it is a diethyl derivative:

	Calculated for $C_{13}H_{19}O_2N$.	Found. I.	II.
N	6.33	6.43	6.30

After boiling this material for 5 hours with alcoholic potassium hydroxide, evaporating to dryness with acetic acid and extracting the residue with petroleum ether the material was recovered unaltered. The substance is therefore a N-diethyl acid and not an ester. It is unaffected by boiling acetic anhydride, is readily soluble in water, ethyl acetate, benzene, chloroform, alcohol and acetone, and dissolves with difficulty in ether and petroleum ether. In the latter solvent it gives a beautiful, sky-blue fluorescence.

3,5-Dimethyl-2-ethylaminobenzoic Acid.—The residue remaining undissolved in petroleum ether was taken up in a small amount of hot water. Upon standing in a desiccator for some time, large, colorless prisms, melting at 190° with effervescence, separated. The first crop of these crystals weighed 1.0 gram. That we were not dealing with unaltered acid, which has the same melting point, was shown by mixing the substance with the original acid. The mixture melted at 162°.

	Calculated for $C_{11}H_{15}O_2N$.	Found.
N	7.25	7.35

Alcoholic potassium hydroxide has no effect on the substance.

2-Nitro-5-methylbenzoic Acid, $C_6H_2\begin{cases}\text{COOH}(1)\\ \text{NO}_2\ (2)\\ \text{CH}_3\ (5)\end{cases}$.—*m*-Toluic acid was nitrated according to Jacobsen's directions.[1] In one experiment 65 grams of the acid were added to 300 cc. of fuming nitric acid (sp. gr. 1.5). After pouring into water the product was converted into barium salts. The first crop of crystals that separated from water weighed 25 grams and the acid precipitated from this (18 grams) melted at about

[1] *Loc. cit.*

182°, the melting point given by Jacobsen for his so-called 2-nitrotoluic acid,[1] or β-nitro-*m*-toluic acid, $C_6H_3{}^{1}CH_3{}^{4}.NO_2{}^{3}.CO_2H$.

This was found to be a mixture, since on crystallizing only once from alcohol stout prisms, melting at 219°, were obtained. This material is 2-nitro-5-methylbenzoic acid. From the mother liquor, on standing, prisms, and finally fine needles, separated. On gently warming the solution the needles easily dissolved, leaving the prisms. The whole material was therefore crystallized from alcohol, and from the final mother liquor the needles were separated mechanically from the prisms. On crystallizing from alcohol they melted at 211°, the melting point of *3-methyl-4-nitrobenzoic acid*. A portion was warmed with phosphorus pentachloride and poured upon ammonium carbonate. The amide obtained melted at 151°, crystallized in plates, and agreed in every respect with the amide of 3-methyl-4-nitrobenzoic acid prepared in a different manner by Beilstein and Kreusler.[2]

2-Nitro-5-methylbenzamide, from the above acid melting at 219°, crystallized from alcohol in large, transparent prisms melting at 190°. It is moderately soluble in hot water and readily soluble in alcohol.

	Calculated for $C_8H_{10}O_3N_2$.	Found.
N	15.38	15.31

2-Amino-5-methylbenzoic Acid.—Jacobsen reduced the nitro acid melting at 219° with tin and hydrochloric acid. When we tried this method we found that the yield of amino acid was only about 25 per cent., the greater part of the material being converted into *p*-toluidine. By using ferrous sulphate and ammonia in the usual manner, the yield of amino acid was increased to over 90 per cent. of the calculated. This property of substituted nitrobenzoic acids of giving off the carboxyl group, when reduced with tin and hydrochloric acid, is a frequent cause of poor yields.

Ethylation of 2-Amino-5-methylbenzoic Acid.

2-Ethylamino-5-methylbenzoic Acid.—Four grams of the

[1] Beilstein: Handbuch, [3] **2**, 1337.
[2] Ann. Chem. (Liebig), **144**, 168.

above amino acid, melting at 170°–171°, were warmed in alcoholic solution with potassium hydroxide and ethyl iodide for six hours and then evaporated to dryness. After treating the residue with water and dilute ammonia it weighed 0.4 gram. This represented the amount of primary amino ester formed, since on saponification the unaltered acid was obtained.

On acidifying the aqueous solution, nothing separated. It was evaporated to dryness, the residue extracted with ethyl acetate, the ethyl acetate evaporated and the residue left extracted with ligroin. Large, transparent prisms, melting to an oil at 71°–72°, separated. The yield was about 3 grams.

	Calculated for $C_{11}H_{15}O_2N$.	Found.
N	7.82	7.88

This acid is readily soluble in water, alcohol, benzene and chloroform, and difficultly soluble in ligroin, in which it shows a sky-blue fluorescence. It remained unaltered when boiled with alcoholic potassium hydroxide.

2-Diethylamino-5-methylbenzoic Acid.—Upon concentrating the ligroin solution by spontaneous evaporation a substance separated that was more soluble than the above monoethyl acid. It crystallized from ligroin in long, fine needles, melting to an oil at 55°–57°. When mixed with the monoethyl acid it melted at 48°–50°. The amount of this material obtained was about 0.2 gram and it was probably the N-diethyl derivative.

	Calculated for $C_{12}H_{17}O_2N$.	Found.
N	7.13	7.23

From the ammonia solution 0.4 gram of unaltered acid was obtained.

2-Amino-3-iod-5-methylbenzoic Acid.—Three grams of iodine monochloride were added to a solution of 2.7 grams of 2-amino-5-methylbenzoic acid in a small amount of dilute hydrochloric acid and the mixture was warmed for an hour on the steam bath. A crystalline substance separated on warming; this was filtered, dissolved in ammonia, some sodium bisulphite

added, and then the solution acidified with acetic acid. The flesh-colored precipitate that separated weighed 3.8 grams, or 75 per cent. of the calculated. It was readily soluble in alcohol, difficultly in water, and moderately soluble in glacial acetic acid. It formed square plates from acetic acid and prisms from alcohol, which melted with decomposition at 212°.

	Calculated for $C_8H_8O_2NI$.	Found. I.	II.
N	5.06	5.15	5.05

Ethylation of 2-Amino-3-iod-5-methylbenzoic Acid.

Ethyl 2-Amino-3-iod-5-methylbenzoate.—The ethylation in this case was carried out in the usual manner with 4.8 grams of the above acid and the solution was warmed for two hours. The residue, on treating with water, left an oil which solidified in a freezing mixture. A portion dissolved when treated with dilute ammonia. The undissolved portion was dried over sulphuric acid; it weighed 1.5 grams. It was readily soluble in alcohol and petroleum ether; from the latter it formed long, colorless prisms, melting to an oil at 70°–71°.

	Calculated for $C_{10}H_{12}O_2NI$.	Found.
N	4.60	4.76

On saponification it gave the unaltered acid.

Acetic acid precipitated 0.5 gram of unaltered acid from the aqueous extract.

2-Diethylamino-3-iod-5-methylbenzoic Acid.—When the ammonia solution was acidified with acetic acid 2.4 grams of unaltered acid were obtained. The solution was then evaporated to dryness, whereupon a small amount of sticky residue remained. This was extracted with petroleum ether and on concentrating the solution 0.4 gram of fine, hairlike crystals, which melted to an oil at 125°–126°, separated. This material was moderately soluble in petroleum ether and rather difficultly soluble in cold water.

	Calculated for $C_{12}H_{16}O_2NI$.	Found.
N	4.20	4.10

Alcoholic potassium hydroxide had no effect on the substance.

NEW HAVEN, CONN.
May, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

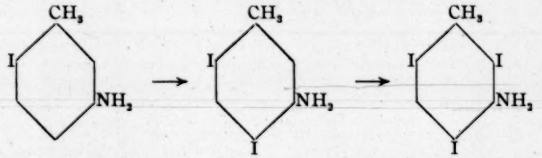
CLXXXII.—ON THE ACTION OF IODINE ON META-TOLUIDINE.

BY HENRY L. WHEELER.

EXPERIMENTAL WORK BY CHARLES A. BRAUTLECHT, CHARLES HOFFMAN AND SAMUEL R. SCHOLES.

In previous papers[1] we have shown that when *p*-toluidine is mixed with iodine a mono- and a diiod derivative can easily be obtained, while under the same conditions *o*-toluidine yields a monoiod compound.

In the present paper we describe the compounds obtained by the action of iodine on *m*-toluidine. In this case the tendency of the base to take up iodine is most pronounced and at least the three following compounds are formed:



I. II. III.

With the quantities of *m*-toluidine employed by us, no other iodine derivatives were isolated. It is probable that isomeric products are produced in small amounts in this reaction; some 4-iod-*m*-toluidine and also 2,6-diiod-*m*-toluidine might be expected. The 6 position is the first point of attack, as in the case of the action of bromine, nitric acid, etc.

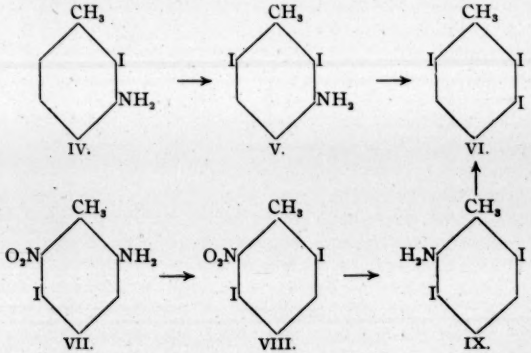
6-Iod-*m*-toluidine (I) has been obtained by Artmann[2] by an indirect method. The other derivatives are new. Their structure was determined as follows: 4-Iod-*m*-toluidine[3]

[1] Wheeler and Liddle: THIS JOURNAL, **42**, 441, 489 (1909).

[2] Monats. Chem., **26**, 1099 (1905).

[3] From 3-nitro-4-iodtoluene. Willgerodt and Simonis: Ber. d. chem. Ges., **39**, 269 (1906).

and 6-iod-*m*-toluidine, when mixed with iodine, gave the 4,6-diiod compound (II), while this compound and 2,6-diiod-*m*-toluidine gave the same triiod-*m*-toluidine (III). The new 2,6-diiod-*m*-toluidine (V below) was prepared from 2-iod-*m*-toluidine (IV)[1] by treating the acetyl compound of the latter base with iodine monochloride and then saponifying. That this procedure produced 2,6-diiod-*m*-toluidine was established by first preparing 2,3,6-triiodtoluene (VI) from this base, by diazotizing and replacing the amino group by iodine; and, then again, the same triiodtoluene, melting at 80°.5, was obtained from 2,6-dinitrotoluene. The latter process was carried out as follows: From the dinitrotoluene we prepared 6-nitro-*o*-toluidine by reducing with ammonium sulphide. When this base was treated with iodine it gave 5-iod-6-nitro-*o*-toluidine (VII) and then, on replacing the amino group with iodine, we obtained 2,5-diiod-6-nitrotoluene (VIII), or 2-nitro-3,6-diiodtoluene. This was reduced with ferrous sulphate and ammonia and the resulting 3,6-diiod-*o*-toluidine (IX) was converted into 2,3,6-triiodtoluene in the usual manner. The two methods of preparing this substance, which not only settle the structure of the triiodtoluene but also that of 2,6-diiod-*m*-toluidine, may be represented as follows:



[1] Wheeler and Liddle: THIS JOURNAL, **31**, 452 (1909).

EXPERIMENTAL PART.

The Action of Iodine on m-*Toluidine.*—When *m*-toluidine is mixed with iodine in molecular proportions (1 molecule base : I_2) in the presence of ether, water and an excess of calcium carbonate, a mixture of unaltered toluidine and of mono- and diiodtoluidines is obtained.

The same is true when the base is treated with iodine in the proportion 1 molecule toluidine : I_3.

When the proportion of the reacting substances is 1 molecule base : I_4, the product consists of a mixture of mono-, di- and triiodtoluidines in which the amount of the di-derivative predominates, while one molecular proportion of the base and three of iodine (I_6) give triiodtoluidine and resinous material. The greater the proportion of iodine used the more tar or resin is formed. Iodine determinations were made by Carius' method. If the substances were heated long enough and high enough (near 300°), good results were usually obtained; otherwise the analytical figures were below the calculated.

All of the monoiod derivatives of *m*-toluidine have a disagreeable odor. In the case of 5-iod-*m*-toluidine, which is the only one that is stable on keeping, it is scarcely noticeable, while 4-iod-*m*-toluidine has the most pronounced odor.

A slight impurity decidedly lowers the melting point of these bases, and also that of the iodtoluenes, the lower iodine derivatives remaining liquid when impure. All of the compounds described in this paper liberate iodine when moistened with sulphuric acid and heated. Iodine in the aromatic group appears to be more sensitive towards acids than alkalies.

By Charles Hoffman.

The following experiment illustrates our method of examining the reactions: Ten grams of *m*-toluidine were dissolved in 30 cc. of ether. The solution was placed in a large distilling flask and 35.6 grams of iodine (calculated for I_3), 10 grams of calcium carbonate, and 30 cc. of water, were added. The mixture was heated on the steam bath until the iodine disappeared. The ether was then evaporated and the residue distilled with steam. The first two liters of

distillate contained an oil which did not solidify on cooling. The remaining portions of the distillate gave, on standing, crystalline material which weighed 15 grams and, on crystallizing from alcohol, melted at 73°–74° (4,6-diiod-*m*-toluidine). The oil from the first portions of the distillate was extracted with benzene and treated with acetic anhydride; this gave two acetyl derivatives: 3.5 grams of material melting at 132°–134° (6-iod-*m*-acettoluide), and about one gram of *m*-acettoluide. A black, resinous substance remained in the distilling flask. This was extracted with alcohol, but nothing was obtained. There was therefore no evidence of the formation of triiod-*m*-toluidine. In the above experiment about 8 per cent. of the *m*-toluidine remained unaltered, 14 per cent. was converted into 6-iod-*m*-toluidine and 45 per cent. into 4,6-diiod-*m*-toluidine.

When two molecular proportions of iodine were used (I_4), 24 grams of *m*-toluidine, after 4 hours' heating, gave a little unaltered material, 2.5 grams of monoiodtoluidine, 30.5 grams of diiodtoluidine, 3 grams of triiodtoluidine and resinous material. Eight per cent. of the *m*-toluidine was changed to monoiod-, 38 per cent. to diiod-, and 3 per cent. to triiod-*m*-toluidine.

When three molecular proportions of iodine were used (I_6), ten grams of the base, after 40 hours, gave no unaltered toluidine or mono- or diiodtoluidine on distilling with steam, but, on extracting the black residue with alcohol, 15 grams of triiodtoluidine were obtained, which corresponds to 35 per cent. of the *m*-toluidine employed.

The yields vary to a considerable extent with slight changes of conditions. In another experiment, for example (Brautlecht), 5 grams of *m*-toluidine, when treated with the calculated amount of iodine (I_6) in three portions and not warmed as long, gave 13 grams of the triiod derivative.

6-Iod-m-*toluidine*, $C_6H_3(CH_3)(1)(NH_2)(3)(I)(6)$.—For purposes of comparison this compound was prepared by Artmann's method.[1]

[1] *Loc. cit.*

o-Acettoluide was nitrated[1] and the *5-nitro-o-toluidine* was converted into *2-iod-5-nitrotoluene*. This, on reduction, gave a base which, when purified by distilling in steam and crystallizing from petroleum ether, melted at 37°–39°. Artmann states that the iodtoluidine prepared in this manner melts at 98°–99° and the acetyl derivative at 132°. We have prepared the base by three different methods and in each case it melted at 37°–39° and the acetyl derivative at 132°–134°.

The best method for the preparation of *6-iod*-m-*toluidine* was found to be as follows: Twenty grams of *m*-acettoluide were dissolved in 20 cc. of glacial acetic acid and treated with 22 grams of iodine monochloride (one molecule) and this mixture was heated on a water bath, under a return condenser, for one hour. Upon adding water a dark substance separated, which lost most of its color on shaking with acid sodium sulphite. When crystallized from alcohol, 24.2 grams of 6-iod-*m*-acettoluide, melting at 132°–134°, or 70 per cent. of the calculated amount, was obtained.

In order to obtain the free base from this acetyl compound, 14.2 grams of the latter were dissolved in a small amount of alcohol containing 8.7 grams of potassium hydroxide. After boiling for two hours the alcohol was evaporated and the residue distilled with steam. We obtained 8.85 grams of white crystalline material melting at 37°–39° (74 per cent. of the calculated), the melting point of which did not change when crystallized from petroleum ether.

m-Acettoluide was treated with two molecular proportions of iodine monochloride, but only the above monoiod derivative was obtained. Both *m*-acettoluide and the free base give the same monoiod derivative.

6-Iod-*m*-toluidine crystallizes from petroleum ether in colorless plates which have a disagreeable odor. They soon become brown on standing in the air and decompose, leaving a dark brown oil.

6-Iod-m-*acetaminobenzoic Acid*, $C_6H_2(COOH)(1)(I)(6)-NHCOCH_3(3)$.—

[1] Reverdin and Crépieux: Ber. d. chem. Ges., **33**, 2498.

Twenty-five grams of 6-iod-*m*-acettoluide were suspended in a liter of water and 24 grams of magnesium sulphate were added. This mixture was stirred by passing steam into it and a solution of 30 grams of potassium permanganate in a liter of water was slowly added. After heating 24 hours, the excess of permanganate was removed by adding alcohol. The solution was evaporated to a small volume, filtered and acidified with hydrochloric acid. This gave 14.4 grams of nearly pure acid, or 52 per cent. of the calculated. It was moderately soluble in hot water and crystallized in long, colorless, prismatic needles, which melted to a clear oil at 210°. It was readily soluble in alcohol and was not precipitated from alkaline solutions by acetic acid.

	Calculated for $C_9H_8O_2NI$.	Found.
N	4.59	4.50

In view of the stability of isomeric iodaminobenzoic acids, namely 3-, 4-, or 5-iod-2-amino-, 5-iod-3-amino-, and 5-iod-4-aminobenzoic acids,[1] we were surprised to find that 6-iod-3-aminobenzoic acid from the above acetyl derivative is an extremely unstable substance.

An attempt was made to saponify the acetyl compound with dilute hydrochloric acid. The solution was warmed for about a half hour and then cooled. Colorless needles, which formed burrlike crystals, separated. These were probably the hydrochloric acid salt. They were filtered off and dissolved in ammonia and the solution was acidified with acetic acid; no precipitate was formed, but a dark, inklike solution resulted, and on evaporation a coal-black residue was obtained. This dissolved in alkali, giving a black solution which, on acidifying with hydrochloric acid, turned deep blue and deposited an amorphous, flocculent, blue precipitate.

When the acetyl derivative was saponified by warming with alcoholic potassium hydroxide, the alcohol evaporated, and the aqueous solution acidified, the same result was obtained. It may also be stated that when iodine is added to an

[1] Wheeler and Liddle: THIS JOURNAL, **42**, 456, 499 (1909).

aqueous solution of the potassium salt of *m*-aminobenzoic acid and the solution evaporated, the same result is obtained.

4,6-Diiod-m-*toluidine*, $C_6H_2\begin{cases}CH_3\ (1)\\NH_2\ (3)\\I\ \ (4)\\I\ \ (6)\end{cases}$, from *m*-toluidine, 6-iod-*m*-toluidine, or 4-iod-*m*-toluidine (Scholes) and iodine, crystallizes from alcohol in large, thick, colorless needles or spikes, which turn brown when exposed to the air. It is readily soluble in alcohol, petroleum ether, ether and benzene, and melts to a clear oil at 73°–74°. It forms, with hydrochloric and sulphuric acids, difficultly soluble salts, which are decomposed by water. The hydrochloride crystallizes in long needles from alcohol, but on boiling the solutions vapors of iodine are given off.

	Calculated for $C_7H_7NI_2$.	Found.
N	3.90	3.93
I	70.75	70.93

The *acetyl derivative*, $C_7H_5I_2NHCOCH_3$, is difficultly soluble in alcohol and almost insoluble in water. It forms long, fine, colorless needles melting at 213°.

	Calculated for $C_9H_9ONI_2$.	Found.
N	3.49	3.60

The inertness of this acettoluide towards potassium permanganate is noteworthy. When 11 grams were warmed for seven days with a dilute solution of potassium permanganate and an equal weight of magnesium sulphate only 0.4 gram of material with acid properties, melting at 260°, was obtained. The remaining material was recovered unaltered. In another experiment the material was heated in a closed tube for 4 hours at 200° with a solution of potassium permanganate; even in this case only a small amount was oxidized.

2,4,6-Triiod-m-*toluidine*, $C_6H\begin{cases}CH_3\ (1)\\NH_2\ (3)\\I\ \ (2)\\I\ \ (4)\\I\ \ (6)\end{cases}$.—Three grams of

4,6-diiod-*m*-toluidine were treated with one molecular proportion of iodine in the presence of ether, water, and an excess of calcium carbonate. After heating 8 hours the mixture was filtered and the residue extracted with alcohol. The yield of triiod-*m*-toluidine was 2.8 grams, or 70 per cent. of the calculated.

The material for analysis was prepared from *m*-toluidine and iodine (by Brautlecht) as described above.

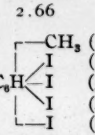
	Calculated for $C_7H_6NI_3$.	Found.
N	2.89	2.91
I	78.56	78.29

This triiodtoluidine was also prepared by the action of iodine on 2,6-diiod-*m*-toluidine (Brautlecht, below). This settles the structure of the compound and that of the following derivatives:

2,4,6-Triiod-*m*-toluidine crystallizes from alcohol, in which it is quite difficultly soluble, in the form of long, pale brown, hairlike needles, which melt sharply to an oil at 135°. Further crystallization from alcohol did not alter the melting point or remove the color. It does not form salts with aqueous acids.

2,4,6-Triiod-m-*acettoluide*, $C_7H_4I_3NHCOCH_3$.—When the above triiodtoluidine was warmed on the steam bath with acetic anhydride no reaction took place. Two grams of the base were warmed on the steam bath for 2 hours with an excess of acetyl chloride. This gave the acetyl compound. It is moderately soluble in alcohol and crystallizes in radiating clusters of needles, which melt to a dark oil at 265°.

	Calculated for $C_9H_8ONI_3$.	Found.
N	2.66	2.83

2,3,4,6-Tetraiodtoluene, 
.—Five grams of 2,4,6-triiod-*m*-toluidine were dissolved in 15 cc. of concentrated sulphuric acid, cooled in a freezing mixture. To the deep

purple solution 1.8 grams of dry powdered sodium nitrite (2 molecules) were added. The mixture was then poured on finely crushed ice. This gave a light lemon-colored diazo solution which was filtered into a solution of 12 grams of potassium iodide in a small amount of ice water. The dark brown diazo iodide which separated was decomposed by warming the solution, and the product was treated with acid sodium sulphite. The material was then almost colorless and weighed 6 grams, or 92 per cent. of the calculated. It was difficultly soluble in alcohol and only moderately soluble in benzene. From the latter solvent it crystallized in long needles and melted to a clear oil at 170°.

	Calculated for $C_7H_4I_2$.	Found.
I	85.23	64.60

By Charles A. Brautlecht.

2,6-Diiod-m-*acettoluide*, $C_6H_2\begin{cases}CH_3 & (1)\\ NHCOCH_3 & (3)\\ I & (2)\\ I & (6)\end{cases}$.—The starting point for the preparation of this compound and the free base was *o*-acettoluide. This was nitrated according to the directions of Reverdin and Crépieux.[1] The *3-nitro-2-aminotoluene* thus obtained was converted into *3-nitro-2-iodtoluene* and this was reduced with ferrous sulphate and ammonia to *2-iod*-m-*toluidine*,[2] melting at 41°–42°. The action of iodine on this base gave a mixture of products, while the acetyl compound and iodine monochloride reacted smoothly. The *2-iod*-m-*acettoluide* (9.8 grams), melting at 135°, was dissolved in a small amount of glacial acetic acid. On adding iodine monochloride (11.6 grams) an immediate reaction took place and heat was evolved. The mixture was warmed for about 5 minutes on the steam bath and then allowed to stand for sixteen hours. Crystals separated, and when water was added to the glacial acetic acid solution more of the same material was obtained. It was difficultly soluble in alcohol and formed colorless prisms which melted to a clear oil at

[1] *Loc. cit.*

[2] Wheeler and Liddle: This Journal, **42**, 452 (1909).

171°. The yield in two experiments was 78 per cent. of the calculated.

	Calculated for $C_8H_{11}ONI_2$.	Found.
N	3.49	3.56

2,6-Diiod-m-*toluidine*, $C_6H_2\begin{cases}CH_3\ (1)\\NH_2\ (3)\\I\ (2)\\I\ (6)\end{cases}$.—Nine grams of the above acetyl derivative were saponified by boiling with 3.6 grams potassium hydroxide in alcoholic solution. At the end of two hours the product was distilled in steam, whereby the base slowly distilled over. The first portion of the distillate was oily, while the remainder gave colorless needles and prisms which were crystallized from alcohol and petroleum ether. The material then melted at 88°. The yield was 82 per cent. of the calculated.

	Calculated for $C_7H_7NI_2$.	Found.
N	3.90	3.82

2,6-Diiod-m-*toluidine* gives a hydrochloride which is difficultly soluble in 10 per cent. hydrochloric acid and readily soluble in alcohol. It is decomposed by water.

When this base was treated with one molecular proportion of iodine in ether solution and then warmed on the steam bath the reaction was over in a short time. The product separated from ether in needles melting at 135° and when crystallized from alcohol or mixed with the triiod-*m*-toluidine above, the melting point was not altered. The latter compound is therefore 2,4,6-triiod-*m*-toluidine.

2,3,6-Triiodtoluene, $C_6H_2\begin{cases}CH_3\ (1)\\I\ (2)\\I\ (3)\\I\ (6)\end{cases}$.—Four and six-tenths grams of 2,6-diiod-*m*-toluidine and 1.2 grams of dry sodium nitrite were mixed with 20 grams of concentrated sulphuric acid at 0°. This mixture, treated with crushed ice, formed a diazo solution, leaving only a small amount of undissolved material. This was filtered and added to a solution of 12.8

grams of potassium iodide in ice water. After warming, then treating with sodium bisulphite and cooling, the crystalline mass obtained amounted to 93 per cent. of the calculated. When crystallized from alcohol it was found to be difficultly soluble and formed colorless needles, which melted sharply to a clear oil at 80°.5. It is practically nonvolatile in steam. Two and a half liters of distillate contained about 0.05 gram.

	Calculated for $C_7H_5I_3$.	Found.
I	81.06	81.18

In regard to the structure of the above compounds, it is to be noticed from their method of preparation that iodine is known to be in the 2 and 3 positions. That iodine is also in the 6 position is proved by preparing this triiodtoluene from 2,6-dinitrotoluene.

6-Nitro-o-toluidine, $C_6H_3\begin{cases}CH_3\ (1)\\NH_2\ (2)\\NO_2\ (6)\end{cases}$.—This was prepared by reducing 2,6-dinitrotoluene (Kahlbaum) with ammonium sulphide.[1] As the yield was 96 per cent. of the calculated we give the details: Twenty grams of the dinitrotoluene was mixed with 60 cc. of 95 per cent. alcohol and 50 cc. of concentrated ammonia. Hydrogen sulphide was passed into the mixture for one hour and the solution gently warmed at first. The contents of the flask were transferred to a casserole and the alcohol evaporated. The residue was extracted with hydrochloric acid and precipitated with ammonia. The base melted at 91°.5.

5-Iod-6-nitro-o-toluidine, $C_6H_2\begin{cases}CH_3\ (1)\\NH_2\ (2)\\I\ \ (5)\\NO_2\ (6)\end{cases}$.—Molecular proportions of the above nitrotoluidine and iodine were warmed with ether, water and calcium carbonate for several hours. The ether was evaporated and the residue extracted with boiling alcohol and the material then precipitated from the alcoholic solution by adding dilute ammonia. The yields varied

[1] Cunerth: Ann. Chem. (Liebig), **172**, 223 (1874). Ullmann: Ber. d. chem. Ges., **17**, 1959 (1884). Bernthsen: *Ibid.*, **18**, 3018 (1882).

to a considerable extent; in one case in which we used 20 grams of base, the product was mostly tar or resinous material. When 5 grams or less were used the yields in eight experiments amounted to 70–87 per cent. This iodnitrotoluidine forms, from alcohol, beautiful yellow prisms, which melt sharply to a clear oil at 85°.

	Calculated for $C_7H_7O_2NI$.	Found.
N	10.07	10.04

The action of iodine monochloride on 6-nitro-*o*-toluidine in glacial acetic acid gave a dark brown tar as the chief product.

2,5-Diiod-6-nitrotoluene, $C_6H_2<^{CH_3\ (1)}_{I\ (2)}{}_{I\ (5)}{}^{NO_2\ (6)}$.—Seven grams of the above base were diazotized and treated with potassium iodide as in the case of 2,3,6-triiodtoluene. The yield was almost quantitative. The material is readily soluble in hot alcohol and forms colorless needles, which melt to a clear oil at 105°.

	Calculated for $C_7H_5O_2NI_2$.	Found.
N	3.60	3.56

3,6-Diiod-o-toluidine, $C_6H_2<^{CH_3\ (1)}_{NH_2\ (2)}{}_{I\ (3)}{}^{I\ (6)}$.—Ten and a half grams of the above 2,5-diiod-6-nitrotoluene were reduced by warming for 18 hours at 60°–100° with a mixture of 84 grams of ferrous sulphate, 200 cc. of water, 200 cc. of concentrated ammonia, and a little alcohol. The solution was then filtered and the residue extracted with alcohol. On concentrating, the pure diiodtoluidine separated. The yield was 67 per cent. of the calculated. When crystallized from alcohol it formed colorless needles which melted sharply to an oil at 86°.

	Calculated for $C_7H_7NI_2$.	Found.
N	3.90	3.87

When this material was diazotized, in the manner described above, and treated with potassium iodide a 90 per cent. yield of triiodtoluene was obtained. This triiodtoluene melted at 80°.5, crystallized from alcohol in lustrous needles and proved to be identical with the 2,3,6-triiodtoluene described above. When mixed with this material the melting point was not altered. This proves that 2-iod-*m*-acettoluide iodates in the 6 position and that iodine substitutes in the 3 or 5 position in 6-nitro-*o*-toluidine. The halogens usually take the para position to the amino group. That substitution takes place in the 5 position in this case was shown on removing the amino group from the iod-6-nitro-*o*-toluidine. The base was diazotized in dilute sulphuric acid and the solution was poured into hot alcohol. The mixture was warmed, made alkaline with sodium hydroxide and distilled with steam. A light yellow oil came over which, on cooling, solidified. This was not identical with 3-iod-6-nitrotoluene described by Artmann.[1] It must therefore be 5-iod-6-nitrotoluene, or, in other words, 2-nitro-3-iodtoluene. It formed, from petroleum ether, transparent, colorless, prismatic plates, which melted at 65°.

By Samuel R. Scholes.

4-Iod-m-*toluidine*, $C_6H_3\begin{cases}CH_3\ (1)\\NH_2\ (3)\\I\ (4)\end{cases}$.—*p*-Acettoluide was the starting point for the preparation of this and the following compounds. This was nitrated by the method of Cosack.[2] A cooling mixture is necessary to keep the temperature during the nitration at 20°–30°. The yield of material melting at 93° (3-nitro-*p*-acettoluide) was 85 per cent. of the calculated. The *3-nitro*-p-*toluidine* was prepared from this material by warming with concentrated hydrochloric acid, 3 cc. of acid being used for each gram of acetyl compound. The base then separates on pouring into water, more completely on adding ammonia. It melted at 115°–116°. This base was diazotized and the solution treated with potassium iodide as described in previous cases. The yield of *4-iod-3-nitro-*

[1] Monats. Chem., **26**, 1096.
[2] Ber. d. chem. Ges., **13**, 1088 (1880).

toluene, melting at 55°, was 84 per cent. of the calculated. This was reduced with ferrous sulphate and ammonia as follows: The iodnitrotoluene was treated with 10 times its weight (6.5 molecules) of ferrous sulphate, 20 times its weight of water, and an equal volume of concentrated ammonia. This mixture was allowed to stand at 60° for 12 hours and was then filtered. The residue was extracted with hot alcohol, and on evaporating the alcohol a green oil with a vile odor was obtained. This was distilled with steam and a pale brown oil came over. On cooling a portion below 0° the oil solidified; the remainder could then be induced to solidify at ordinary temperature by adding some of the solid. When this was crystallized from dilute alcohol, long, colorless needles, which melted constantly at 38°–38°.5, were obtained. The pure base has a disagreeable odor suggesting α-naphthylamine. On standing several weeks it changed to a dark oil with a still more noticeable odor.

	Calculated for C_7H_8NI.	Found.
N	6.01	5.95
I	54.80	54.56

In Beilstein's *Handbuch*[1] a substance is given, subject to interrogation, as *4-iod-3-toluidine*, which melts at 188°–189°. This was obtained by Glassner.[2] We have prepared all of the four monoiod derivatives of *m*-toluidine and find that this substance does not agree with any of these compounds. When the work on this base was finished we discovered that Willgerodt and Simonis[3] had also prepared the compound by reducing 4-iod-3-nitrotoluene with ferrous sulphate. They give its melting point as 48°.

The *hydrochloride*, $C_7H_8NI.HCl$, is difficultly soluble in dilute hydrochloric acid, easily in hot alcohol, and undergoes hydrolysis in water. It decomposes on heating at 155° (Willgerodt and Simonis, 90°–150°).

	Calculated for $C_7H_8NI.HCl$.	Found.
N	5.19	5.12

[1] [3] **2**, 475.
[2] Ber. d. chem. Ges., **8**, 561.
[3] *Ibid.*, **39**, 273 (1906).

The *thiourea derivative*, $C_6H_3.I.CH_3NHCSNHC_6H_5$, was formed on warming molecular quantities of the base and phenyl mustard oil on the steam bath in alcoholic solution. After three crystallizations from alcohol, in which it is difficultly soluble, it melted each time at 162°–163°.

	Calculated for $C_{14}H_{13}N_2IS$.	Found.
N	7.61	7.52

4-Iod-m-*acettoluide*, from the base and acetic anhydride, crystallized from alcohol in small, colorless, square-ended prisms melting at 151° (145°–146°, Willgerodt and Simonis). It is only slightly soluble in water.

	Calculated for $C_9H_{10}ONI$.	Found.
N	5.09	4.93

Action of Iodine Monochloride.—This acetyl derivative was mixed with the calculated quantity of iodine monochloride in glacial acetic acid and the solution warmed for a few minutes. The crystals which separated on cooling were recrystallized from alcohol. The material then melted at 213° and proved to be identical with the diiodacettoluide above, prepared by Hoffman. This shows that the compound is 4,6-diiod-*m*-acettoluide.

Action of Iodine on 4-Iod-m-*toluidine.*—Seven and seventenths grams of 4-iod-*m*-toluidine, 8.4 grams of iodine, 4 grams of calcium carbonate, 20 cc. ether and 10 cc. of water were mixed and warmed until the iodine disappeared. The product was then distilled in steam, whereupon 7.5 grams, or 63 per cent. of the calculated, of diiodtoluidine was obtained. On crystallizing from alcohol it melted at 73°–74° and when mixed with Hoffman's diiodtoluidine the melting point was not altered. From these experiments it is evident that in both 4-iod-*m*-acettoluide and the free base the iodine is substituted in the 6 or para position to the amino group.

3,4,6-Triiodtoluene, $C_6H_2\begin{cases}CH_3 & (1)\\ I & (3)\\ I & (4)\\ I & (6)\end{cases}$, was prepared from 4,6-

diiod-*m*-toluidine by diazotizing and treating with potassium iodide as described in previous cases. It was difficult to diazotize the material by this method, owing to the insolubility of the sulphate. Ten grams of the base (not completely diazotized) gave 7 grams of triiodtoluene, or 60 per cent. of the calculated. It formed, from alcohol, long, slender, sharp-pointed, brownish needles, which melted to an oil at 119°-120°. It is almost completely nonvolatile in steam.

	Calculated for $C_7H_5I_3$.	Found.
I	81.06	80.80

3-Nitro-5-iod-p-*toluidine*, $C_6H_2\begin{cases}CH_3 (1)\\NH_2 (4)\\NO_2 (3)\\I (5)\end{cases}$.—Thirty grams of 3-nitro-*p*-toluidine and 48 grams of iodine monochloride were mixed in 100 cc. of glacial acetic acid and warmed on the steam bath for 20–30 minutes. A better yield was obtained on warming than on standing. Water and bisulphite were added, whereupon a golden brown precipitate resulted. When this was crystallized from alcohol golden brown needles separated. They melted at 98°. The yield was 35 grams, or 68 per cent. of the calculated.

	Calculated for $C_7H_7O_2N_2I$.	Found.
N	10.09	9.93

The position of the iodine in this compound was determined by acetylating the base. Acetic anhydride had no action, but when 1 gram of the base was treated with 2 cc. of acetyl chloride the mixture evolved heat and a white product was obtained, which, when crystallized from alcohol, gave colorless needles melting at 202°–203°. These proved to be identical with the iodnitro-*p*-acettoluide prepared by Wheeler and Liddle[1] by nitrating 3-iod-*p*-acettoluide. This settles the structure of this compound, which was left subject to interrogation in our previous paper.

[1] This Journal, **42**, 449 (1909).

3-Nitro-4,5-diiodtoluene, $C_6H_2<^{CH_3\ (1)}_{NO_2\ (3)}_{I\ (4)}_{I\ (5)}$.—This was prepared by diazotizing the above base and treating with potassium iodide in the usual manner. It crystallized from alcohol in orange, rectangular prisms, melting at 84°–85°. The yield was 14 grams, or 64 per cent. of the calculated.

	Calculated for $C_7H_5O_2NI_2$.	Found.
N	3.59	3.39
I	65.29	64.02

This compound is volatile with steam.

*4,5-Diiod-*m*-toluidine,* $C_6H_2<^{CH_3\ (1)}_{NH_2\ (3)}_{I\ (4)}_{I\ (5)}$.—The above diiodnitrotoluene (15 grams) was reduced with the calculated quantity of ferrous sulphate and an excess of ammonia by five hours' treatment at 60°. The black residue was then extracted with alcohol and an attempt was made to distil the extract in steam, but the base was not sufficiently volatile. The whole was gathered together in ether, dried over potassium hydroxide and the base was precipitated by passing dry hydrogen chloride into the solution. The gray-white precipitate (4.1 grams), after washing with ether, dissolved with difficulty in 95 per cent. alcohol and crystallized slowly in bunches of needles. The addition of a few drops of concentrated hydrochloric acid to the solution produced a more complete separation. On treating this hydrochloride with dilute ammonia the base was obtained as an oil which soon solidified. It was separated from traces of tar by repeated crystallization from dilute alcohol. It formed an extremely bulky mass of colorless, cottonlike needles, which finally melted to an amber-colored oil at 66°–67°.

	Calculated for $C_7H_7NI_2$.	Found.
N	3.90	3.67

This base was converted by the action of iodine into an amorphous brown-black substance, which had no definite melting point. The product was neither a tri- nor tetraiodtoluidine.

4,5-Diiod-m-*acettoluide*, $C_6H_2CH_3I_2NHCOCH_3$, from the base and acetyl chloride, is very difficultly soluble in water and readily in alcohol. It formed short, colorless needles, melting at 183°–184°, when repeatedly crystallized from alcohol (analysis I).

	Calculated for $C_9H_9ONI_2$.	Found. I.	II.
N	3.50	3.22	3.84

When this acetyl derivative was treated with the calculated quantity of iodine monochloride in glacial acetic acid and allowed to stand overnight, unaltered material separated. It formed needles as before and melted at 183°–184° after crystallizing from alcohol.

When warmed (2.2 grams) in glacial acetic acid with an excess of iodine monochloride (5ICl), the material obtained had a different appearance. On crystallizing from alcohol it then separated in small diamond-shaped blocks which melted at 200°–201°. Two more recrystallizations failed to change the melting point. A nitrogen determination (analysis II by Brautlecht) indicated that it was a diiodacettoluide, or unaltered material.

We have prepared all of the six theoretically possible diiod-*m*-acettoluides, with the exception of 2,4-diiod-*m*-acettoluide. 2,6-Diiod-*m*-acettoluide melts at 171°; 2,5-diiod-*m*-acettoluide at 198°;[1] 4,6-diiod-*m*-acettoluide at 213°, and 5,6-diiod-*m*-acettoluide at 208°.[1] When the last three isomers were mixed with the above material, melting at 200°, the mixture in each case melted below 175°. This shows that the substance did not undergo a rearrangement into any of these isomers. Whether or not the lower melting point (183°–184°) was caused by some impurity which tenaciously adhered to the material will have to be decided later. The amount of substance melting at 200° was too small for saponi-

[1] To be described in a following paper.

fication and subsequent purification and identification of the base.

3-Nitro-5-iodtoluene, $C_6H_3\begin{cases}CH_3\ (1)\\NO_2\ (3)\\I\ (5)\end{cases}$.—*3,5-Dinitro*-p-*acettoluide* was prepared by the method of Jackson and Ittner[1] and saponified by boiling with 50 per cent. sulphuric acid.

We found that the most convenient method for the removal of the amino group was as follows: Twenty grams of the base were suspended in a mixture of 20 cc. of concentrated sulphuric acid and 150 cc. of absolute alcohol. The mixture was heated on the steam bath and 16 grams of powdered sodium nitrite were slowly added. After heating 30 minutes no red particles of the base were visible. On pouring into water a yellow precipitate separated, which, when crystallized from alcohol, melted at 88°–91°. The yield was 12 grams, or 70 per cent. of the calculated.

The *3,5-dinitrotoluene* thus obtained was reduced to *5-nitro*-m-*toluidine* by means of ammonium sulphide.[2] When this base (9 grams) was diazotized and treated with potassium iodide in the manner described above in other cases, the reaction proceeded smoothly, and, after crystallizing the product from alcohol, 7.5 grams of yellow, rectangular prisms melting at 77° were obtained.

	Calculated for $C_7H_6O_2NI$.	Found.
N	5.34	5.00

5-Iod-m-*toluidine*, $C_6H_3\begin{cases}CH_3\ (1)\\NH_2\ (3)\\I\ (5)\end{cases}$.—Seven and one-half grams of the above nitroiodtoluene, 50 grams of crystallized ferrous sulphate, 200 cc. of water and 200 cc. of concentrated ammonia were mixed and warmed for 24 hours. The mixture was then distilled in steam; an oil came over which readily solidified and dissolved completely in dilute hydrochloric acid. On crystallizing from petroleum ether, long, colorless,

[1] THIS JOURNAL, **19**, 5 (1897).
[2] Neville and Winther: Ber. d. chem. Ges., **15**, 2985.

asbestoslike needles, which melted at 78°–78°.5, were obtained. The yield was about 3 grams.

	Calculated for C_7H_8NI.	Found.
N	6.02	5.89

This iod-*m*-toluidine has a very faint odor, suggesting that of α-naphthylamine, and can be kept for months without change. The acetyl derivative forms micalike plates from alcohol which melt at 183°.

NEW HAVEN, CONN.,
April, 1910.

A STUDY OF THE SURFACE TENSIONS OF SOME UNSATURATED ORGANIC COMPOUNDS.

BY FREDERICK H. GETMAN.

In recent years the attention of workers in this laboratory has been largely directed to the investigation of the chemical behavior of unsaturated organic compounds. As a result of this continued and systematic research many new substances have been prepared and important generalizations have been pointed out.

Notwithstanding the large accumulation of chemical data concerning unsaturated organic compounds, however, very little has been done in the way of determining their physical constants.

The value of the systematic determination of physical constants of organic compounds has already become recognized and we believe that the careful measurement of a number of physical constants of the typical unsaturated compounds which have been studied in this and other laboratories will prove valuable aids to the future study of these interesting substances.

In Stewart's "Recent Advances in Physical and Inorganic Chemistry,"[1] we find the following significant passage at the conclusion of the chapter on Absorption Spectra:[2] "There are two classes of workers whose researches are tending to bring spectroscopy into touch with chemical problems. The

[1] Published by Longmans, Green & Co.
[2] p. 156.

first of these concern themselves with the relation between spectroscopic measurements and other physical properties of organic substances, such as refractive index, optical rotatory power, magnetic rotation, and so forth.

"The second class of investigators endeavor to link their spectroscopic results with their chemical reactions in order to find out whether there be any connection traceable between the two phenomena.

"In either of these directions there appears to be a fruitful field awaiting research."

It is our opinion that what has been said of spectroscopy and its relation to chemical problems is equally applicable to any other line of physical measurement. Before any trustworthy relations can be established a large amount of physical data must be collected and any attempts at generalization must be made with caution.

Through the work of Ramsay and Shields,[1] Ramsay and Aston,[2] Renard and Guye,[3] and others, the importance of surface tension measurements as a criterion of molecular complexity has been emphasized.

It has seemed advisable therefore to undertake a systematic investigation of the surface tensions of a series of closely related unsaturated organic compounds.

The substances which have been studied are mesityl oxide, β-dimethylacrylic acid, benzalacetone, benzalmethylethyl ketone, and benzalpinacolin.

Method and Apparatus.

(*a*) *Surface Tension.*—The surface tension of a liquid, expressed in dynes per centimeter, may be obtained by means of the familiar formula

$$\gamma = 1/2hrg(d-\sigma) \qquad (1),$$

where h = capillary elevation in centimeters,
r = radius of capillary in centimeters,
d = density of liquid,
σ = density of vapor of liquid,
g = acceleration due to gravity.

[1] Z. physik. Chem., **12**, 433 (1893).
[2] *Ibid.*, **15**, 89 (1894).
[3] J. chim. phys., **5**, 81 (1907).

Except for measurements of extreme precision the density of the vapor of the liquid may be omitted and the formula may be written thus:

$$\gamma = 1/2hrdg \qquad (2).$$

The capillary method for the determination of surface tension has been used with success by numerous investigators, among whom may be mentioned Ramsay and Shields, Renard and Guye, and Przyluska.[1]

The apparatus which I have employed in this investigation is a modified form of that used by Mlle. Przyluska. The assembled apparatus is shown in Fig. I. The capillary tube *C*, having been carefully selected so as to insure as uniform bore as possible, was supported by means of a piece of glass rod, *D*, bent as shown in the illustration. The rod was sealed to the side of *C*, thus preventing drops of condensed liquid from closing the upper end of the capillary. The rod *D* passed tightly through a hole in the stopper closing the test tube *B*. Through this same stopper passed a thermometer, *F*, and a tube, *E*, bent at right angles. By blowing gently through *E* the liquid in *B* could be forced up into the capillary, thus insuring thorough wetting of the walls before reading the elevation. The tube *B* was placed inside the vapor jacket *A*, in which various liquids were boiled, thus maintaining *B* and its contents at a definite temperature. The side tube *G* served to connect the vapor jacket with a condenser.

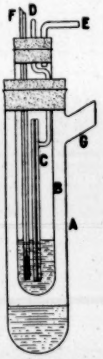


Fig. I.

The capillary elevation of the liquid was measured by means of a cathetometer. By means of a plummet the capillary tube was rendered as nearly vertical as possible.

The following liquids were used in the vapor jacket:

	Boiling point.		Boiling point.
Acetone	55°	Xylene (commercial)	135°
Methyl alcohol	66°	Brombenzene	155°
Benzene	80°	Aniline	182°
Toluene	109°	Methyl benzoate	199°
Amyl formate	116°	Acetophenone	202°

[1] Przyluska: J. chim. phys., **7**, 511 (1909).

The calibration of the capillary was effected with pure benzene, obtained from Kahlbaum, warranted to be free from thiophene. The capillary was first washed with concentrated nitric acid and then with potassium hydroxide, after which it was washed with chromic acid and then with conductivity water. The tube was dried by means of a slow current of air bubbled through concentrated sulphuric acid.

About 10 cc. of benzene were introduced into the tube *B* and after the apparatus had acquired room temperature, readings of the temperature and capillary elevation were taken at frequent intervals during half an hour.

The capillary elevation was then determined in the vapors of boiling acetone and of boiling methyl alcohol, the readings being repeated over a period of several hours. The surface tension and the density of benzene at several temperatures was obtained from the tables of Landolt and Börnstein and the measurements of Ramsay and Shields, Ramsay and Aston, Renard and Guye, and Morgan and Stevenson.[1] Taking the value of g, the acceleration due to gravity, to be 980.2, the value of r was calculated by means of the formula

$$r = \frac{2\gamma}{hdg} \qquad (3).$$

The results of the calibration are given in Table I, each value of h being the mean of several determinations. The mean value of the radius of the tube, 0.02241 cm., was checked by the well-known method of weighing out with mercury, and the agreement was satisfactory:

Table I.

Temp.	h.	d.	γ.	r.
22°.0	2.91	0.8755	27.83	0.02229
57°.0	2.53	0.8376	23.37	0.02251
64°.5	2.46	0.8295	22.42	0.02242
			Mean,	0.02241

(*b*) *Density.*—The densities have been determined by means of a weight dilatometer shown in Fig. II. The dilatom-

[1] Z. physik. Chem., **63**, 151 (1908).

eter, nearly filled with mercury, was placed in the vapor jacket shown in Fig. I. When the mercury and dilatometer had acquired the temperature of the surrounding vapor, more mercury was added until the level of the mercury column remained coincident with the mark *M* on the stem of the dilatometer.

Fig. II.

At least half an hour was allowed for the establishment of thermal equilibrium. The dilatometer was then removed from the vapor jacket and allowed to cool to the temperature of the room. It was then placed in a tared beaker on the pan of the balance and, after acquiring the temperature of the balance case, was weighed.

The density of mercury at the temperature of the vapor jacket was obtained from the tables of Landolt and Börnstein. Having the mass of the mercury in the dilatometer and knowing its density, the volume of the dilatometer at the temperature of the vapor jacket was calculated. Similarly for a series of temperatures the corresponding volumes of the dilatometer were determined. The results of this calibration are given in Table II, in which m denotes the mass of mercury in the dilatometer, d the density of the mercury, and v the volume corresponding to the temperature given in the first column:

Table II.

Temp.	m.	d.	v = m/d.
18°.0	39.3215	13.5511	2.9017
111°.0	38.7490	13.3259	2.9078
122°.5	38.6765	13.2984	2.9085
155°.0	38.4837	13.2212	2.9111
197°.0	38.2415	13.1219	2.9143

In the determination of densities with the weight dilatometer the process was identical with that used in the calibration.

The substance was placed in the dilatometer and brought to the mark at the different temperatures, the dilatometer being weighed after adjustment for each temperature. From the calibration curve the volume corresponding to each temperature could be read off and the density thus calculated.

In the case of mesityl oxide, which is a liquid at ordinary

temperatures, the Sprengel-Ostwald pycnometer was used for density determinations. The densities were calculated by means of the formula

$$d_{4^\circ}^{t^\circ} = \frac{w_1}{w_2}(Q - 0.0012) + 0.0012 \qquad (4),$$

where $d_{4^\circ}^{t^\circ}$ = density of liquid at t° referred to water at 4°,
w_1 = weight of liquid,
w_2 = weight of equal volume of water,
Q = density of water at t°,
0.0012 = density of air.

(*c*) *Temperature.*—All of the thermometers used in this investigation were carefully compared with Reichsanstalt standard No. 5771 and proper corrections were introduced where necessary.

Calculation of Association.—It has been shown by Ramsay and Shields[1] that the molecular surface tension of a liquid is given by the formula

$$\gamma(Mv)^{\frac{1}{4}} = k(t_c - t - 6) \qquad (5),$$

where M denotes the molecular weight, v the volume of a gram of the liquid at the temperature of the experiment, t_c the critical temperature, t the temperature of the experiment, and k the coefficient of variation of molecular surface tension, which has been shown to be about 2.12 for normal or non-associated liquids. The coefficient k may be calculated from the surface tension data at two different temperatures, thus:

$$k = \frac{\gamma_1(Mv_1)^{\frac{1}{4}} - \gamma_2(Mv_2)^{\frac{1}{4}}}{t_2 - t_1} \qquad (6);$$

or substituting $1/d$ for v, where d is the corresponding density, we have

$$k = \frac{\gamma_1\left(\frac{M}{d_1}\right)^{\frac{1}{4}} - \gamma_2\left(\frac{M}{d_2}\right)^{\frac{1}{4}}}{t_2 - t_1} \qquad (7).$$

Should the value of k be less than 2.12 it is an indication of

[1] *Loc. cit.*

molecular association. The degree of association, x, may be calculated by means of the formula

$$x = \left(\frac{2.12}{k}\right)^{3/2} \qquad (8).$$

Materials.—The substances used in this investigation have already been mentioned. They were mesityl oxide, β-dimethylacrylic acid, benzalacetone, benzalmethylethyl ketone and benzalpinacolin. With the exception of mesityl oxide all of these substances are solids at ordinary temperatures. The mesityl oxide was purified by vacuum distillation until no residue remained in the distilling flask. The other substances were purified by careful vacuum distillation and subsequent recrystallization. The recrystallization was repeated until hardly a trace of yellow color remained. It gives me pleasure to acknowledge my indebtedness to Professor E. P. Kohler for the preparation and purification of these substances. After the four solid substances had been purified their melting points were very carefully determined. In each case enough material was taken to give about 10 cc. of liquid when melted. The substance was placed in a test tube fitted with a ring stirrer and a thermometer, and the whole placed in a large beaker of water, also furnished with a stirrer and thermometer. The water was warmed by means of a Bunsen burner until the substance in the test tube had fused, when the source of heat was removed and the system was allowed to cool, both stirrers being agitated simultaneously. The thermometer was read at frequent intervals until the mass solidified and a constant temperature was attained. In all cases there was overcooling to the extent of about 1°. The following melting points were obtained:

	Melting point.
β-Dimethylacrylic acid	69°.2
Benzalacetone	40°.2
Benzalmethylethyl ketone	37°.5
Benzalpinacolin	39°.5

Tabulation of Results.—The results obtained are recorded in the following tables. Tables III–VII, inclusive, give the den-

sities of the five substances investigated. In Tables III and IV the densities actually determined are recorded, while Tables V, VI and VII are compiled from the smoothed curve plotted (Fig. III) from the experimental data. Tables VIII-XVII contain the surface tension data. In

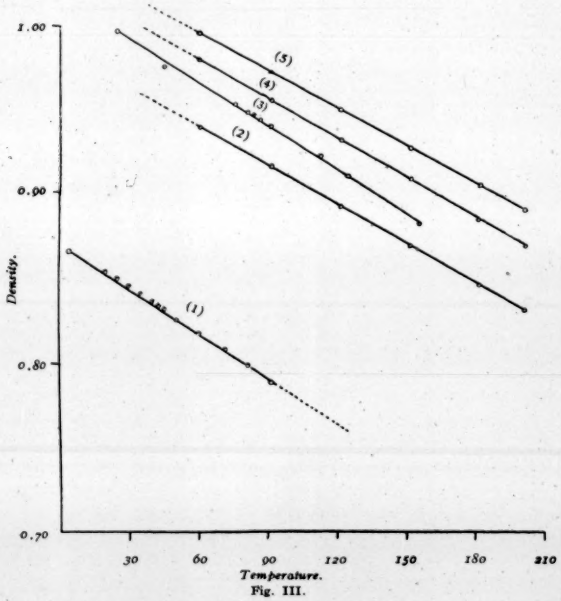


Fig. III.

(1) Mesityl oxide. (2) Benzalpinacolin. (3) β-Dimethylacrylic acid. (4) Benzalmethylethyl ketone. (5) Benzalacetone.

these tables h denotes the observed capillary elevation in centimeters, d the density, γ the surface tension in dynes per centimeter, and k_1 and k_2 the coefficient of variation of molecular surface tension calculated by means of

equation (7). In the calculation of these coefficients two methods have been followed. In the first method, the coeffi-

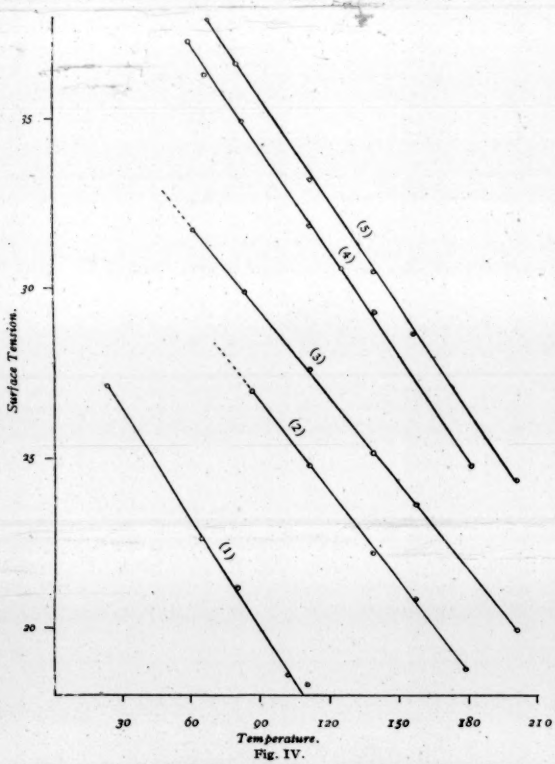


Fig. IV.

(1) Mesityl oxide. (2) β-Dimethylacrylic acid. (3) Benzalpinacolin. (4) Benzalmethylethyl ketone. (5) Benzalacetone.

cient k_1 was obtained by taking the difference between consecutive molecular surface tensions and dividing by the tem-

perature interval between which the capillary elevations were measured: in the second method the coefficient k_2 was obtained by taking the difference between each molecular surface tension and the first molecular surface tension in the table and dividing by the corresponding temperature interval. It will be observed that the value of the coefficient obtained by the second method is more nearly constant than that obtained by the first method. This same observation was made by Mlle. Przyluska[1] in her investigation of the molecular complexity of diphenylamine and triphenylmethane. In Table XI, where k_1 and k_2 are considerably smaller than 2.12, the molecules are associated. The extent of this association x is calculated by means of equation (8).

The surface tensions are plotted in Fig. IV.

Table III.—Mesityl Oxide, $(CH_3)_2C : CHCOCH_3$.

Temp.	d.	Temp.	d.	Temp.	d.
5°.0	0.8662	35°.0	0.8422	50°.0	0.8267
20°.2	0.8545	40°.0	0.8385	60°.0	0.8189
25°.0	0.8510	42°.5	0.8357	70°.0	0.8091
30°.0	0.8462	45°.0	0.8332	80°.0	0.7998
				90°.0	0.7898

Table IV.—β-Dimethylacrylic Acid, $(CH_3)_2C : CH.CO_2H$.

Temp.	d.	Temp.	d.	Temp.	d.
24°.4	1.0062	80°.0	0.9481	95°.0	0.9360
25°.0	0.9959	82°.0	0.9474	111°.0	0.9225
45°.0	0.9750	85°.0	0.9438	122°.5	0.9115
75°.0	0.9538	90°.0	0.9409	154°.0	0.8825

Table V.—Benzalacetone, $C_6H_5.CH : CH.CO.CH_3$.

Temp.	d.	Temp.	d.	Temp.	d.
60°	0.9947	110°	0.9573	160°	0.9202
70°	0.9871	120°	0.9500	170°	0.9129
80°	0.9796	130°	0.9424	180°	0.9054
90°	0.9721	140°	0.9352	190°	0.8981
100°	0.9648	150°	0.9278	200°	0.8908

[1] *Loc. cit.*

Table VI.—Benzalmethylethyl Ketone, $C_6H_5.CH : CH.CO.C_2H_5$.

Temp.	*d.*	Temp.	*d.*	Temp.	*d.*
50°	0.9867	100°	0.9478	150°	0.9087
60°	0.9789	110°	0.9399	160°	0.9010
70°	0.9710	120°	0.9321	170°	0.8932
80°	0.9630	130°	0.9243	180°	0.8856
90°	0.9553	140°	0.9165	190°	0.8775
				200°	0.8697

Table VII.—Benzalpinacolin, $C_6H_5.CH : CH.CO.C(CH_3)_3$.

Temp.	*d.*	Temp.	*d.*	Temp.	*d.*
60°	0.9394	110°	0.9009	160°	0.8623
70°	0.9318	120°	0.8932	170°	0.8547
80°	0.9240	130°	0.8855	180°	0.8470
90°	0.9162	140°	0.8779	190°	0.8392
100°	0.9087	150°	0.8701	200°	0.8341

Table VIII.—Mesityl Oxide, $(CH_3)_2C : CHCOCH_3$.

Temp.	*h.*	*d.*	*r.*
24°.0	2.90	0.8515	27.12
64°.5	2.53	0.8145	22.63
79°.0	2.41	0.8005	21.17
100°.0	2.19	0.7800	18.56
108°.5	2.16	0.7712	18.29
122°.0	1.92	0.7590	16.01

Table IX.

Temp.	*r* (corrected).	k_1.	k_2.
20°	27.55	....	....
40°	25.35	2.23	2.23
60°	23.15	2.18	2.20
80°	20.95	2.27	2.22
100°	18.76	2.30	2.24
120°	16.55	2.42	2.28
	Mean,	2.28	2.22

Table X.—β-Dimethylacrylic Acid, $(CH_3)_2C : CH.CO_2H$.

Temp.	*h.*	*d.*	*r.*
85°	2.60	0.9450	26.98
110°	2.45	0.9220	24.80
137°	2.25	0.8980	22.19
155°	2.15	0.8820	20.83
177°	1.98	0.8620	18.74

Table XI.

Temp.	r (corrected).	k_1.	k_2.	x.
85°	26.98	....	....	....
110°	24.75	1.61	1.52	1.52
137°	22.33	1.71	1.38	1.38
155°	20.70	1.77	1.31	1.31
137°	18.74	1.78	1.29	1.29

Table XII.—Benzalacetone, $C_6H_5CH : CH.CO.CH_3$

Temp.	k.	d.	r.
60°.0	3.53	0.9947	38.53
67°.8	3.49	0.9889	37.89
80°.0	3.40	0.9796	36.58
110°.5	3.15	0.9570	33.11
137°.5	2.96	0.9370	30.46
155°.0	2.82	0.9240	28.62
199°.0	2.49	0.8914	24.37

Table XIII.

Temp.	r (corrected).	k_1.	k_2.
60°	38.53	....	....
80°	36.50	2.25	2.25
100°	34.47	2.39	2.34
120°	32.42	2.44	2.39
140°	30.39	2.45	2.39
160°	28.35	2.40	2.42
180°	26.30	2.70	2.44
200°	24.25	2.64	2.47
	Mean,	2.47	2.40

Table XIV.—Benzalmethylethyl Ketone, $C_6H_5.CH:CH.CO.C_2H_5$

Temp.	k.	d.	r.
59°.5	3.46	0.9795	37.21
67°.0	3.39	0.9735	36.24
82°.0	3.30	0.9615	34.84
110°.5	3.08	0.9395	31.78
124°.0	2.99	0.9290	30.51
138°.0	2.90	0.9182	29.24
180°.0	2.55	0.8856	24.79

Table XV.

Temp.	γ (corrected).	k_1.	k_2.
50°	38.05	....	....
80°	35.00	2.46	2.46
100°	32.97	2.55	2.50
120°	30.94	2.55	2.52
140°	28.93	2.60	2.54
160°	26.87	2.73	2.57
180°	24.79	2.82	2.61
		Mean, 2.62	2.53

Table XVI.—Benzalpinacolin, $C_6H_5.CH : CH.CO.C(CH_3)_3$.

Temp.	k.	d.	γ.
62°.0	3.08	0.9380	31.70
83°.0	2.95	0.9216	29.86
110°.3	2.79	0.9006	27.59
137°.1	2.60	0.8800	25.13
156°.0	2.49	0.8654	23.66
199°.0	2.18	0.8320	19.92

Table XVII.

Temp.	γ (corrected).	k_1.	k_2.
60°	31.85	....	....
80°	30.10	2.40	2.40
100°	28.40	2.41	2.41
120°	26.70	2.44	2.42
140°	24.98	2.68	2.48
160°	23.26	2.44	2.48
180°	21.52	2.65	2.50
200°	19.80	2.73	2.53
		Mean, 2.53	2.46

DISCUSSION OF RESULTS.

An inspection of the foregoing tables shows that, with the exception of β-dimethylacrylic acid, all of the substances studied are nonassociated. This conclusion receives confirmation through an application of the empirical formula proposed by Longinescu[1] as a test for molecular association.

If we denote the absolute melting point of a compound by

[1] Ann. Sci Univ. Jassy, 1, 359. J. chim. phys., 1, 289, 296 (1903).

T and its density in the solid state by d, the number n of atoms in the molecule may be computed by means of the formula

$$n = \left(\frac{T}{70d}\right)^2.$$

In like manner n may be calculated by means of the formula

$$n = \left(\frac{T'}{100d'}\right)^2,$$

where T' denotes the absolute boiling point and d' the density at 0°.

The subjoined table gives the value of n calculated by means of Longinescu's formulas and also the value obtained by counting the number of atoms in the chemical formula for a single molecule:

Substance.	Density.	Abs. m. p.	n.	n (calc.).
$(CH_3)_2C : CH.CO.CH_3$	0.8700	403.0 (b. p.)	17	21
$(CH_3)_2C : CH.CO_2H$	0.9590	342.2	15	25
$C_6H_5CH : CH.CO.CH_3$	1.0095	313.2	21	20
$C_6H_5CH : CH.CO.C_2H_5$	0.9965	310.5	24	20
$C_6H_5CH : CH.CO.C(CH_3)_3$	0.9550	312.5	30	22

It will be seen that these results are in complete agreement with those obtained from the surface tension data.

The value of k for the nonassociated compounds is in all cases greater than 2.12, the mean value assigned by Ramsay and Shields.

The average values of k for the four nonassociated substances studied are 2.22, 2.40, 2.53, and 2.46, respectively.

It will also be noticed that the association of β-dimethylacrylic acid slowly decreases with increase in temperature.

Much more data must be collected before it will be possible to establish any connection between the chemical and physical properties of this class of compounds. It is our intention to continue this line of investigation in the near future.

BRYN MAWR COLLEGE,
BRYN MAWR, PA.,
May, 1910.

THE CONDUCTIVITY AND DISSOCIATION OF ORGANIC ACIDS IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES.

By George F. White and Harry C. Jones.

In our preliminary article[1] results were given for the conductivity of several organic acids at temperatures ranging from 0° to 35°. This work has been extended, and complete data are here presented for the conductivity and likewise the dissociation of all the acids worked with.

μ_∞ for Sodium Chloride.—In order to obtain μ_∞ for the organic acids to calculate their dissociation, the method which involves the use of the sodium salts of these acids, based on Kohlrausch's law of the independent migration velocities of ions, was resorted to. Thus, to calculate μ_∞ for acetic acid, for instance, the following equation suffices:

$$\mu_\infty (HOOCCH_3) = \mu_\infty (HCl) + \mu_\infty (NaOOCCH_3) - \mu_\infty (NaCl),$$

in which μ_∞ is the limiting conductivity for each substance. The following table gives the conductivity of sodium chloride solutions between 0° and 35°:

Sodium Chloride.

V.	μ_v 0°.	μ_v 12°.13.	μ_v 25°.	μ_v 35°.
32	57.17	79.69	106.2	128.6
128	59.76	83.96	112.3	137.2
512	62.01	87.54	117.0	142.1
1024	62.80	88.58	118.4	143.7
2048	*63.04	88.98	*118.8	*144.0

The following equation was calculated by means of values marked with an asterisk in the table:

$$\mu_\infty = 63.04 + 2.04t - 0.00823t^2.$$

μ_{2048} at 12°.13 calculated from this equation gave 88.99, while the observed value was 88.98.

μ_∞ for Hydrochloric Acid.—Following is a table which served to give the limiting conductivities of hydrochloric acid.

[1] This Journal, **42**, 520 (1909).

Hydrochloric Acid.

V.	μ_v 0°.	μ_v 14°.82.	μ_v 25°.	μ_v 35°.
128	240.7	326.6	384.9	438.0
512	245.4	332.3	392.0	448.0
1024	343.0	331.0	387.1	444.7

The maximum conductivity was taken as μ_{512}, and varies according to the following equation:

$$\mu_\infty = 245.4 + 6.06t - 0.00776t^2.$$

μ_{512} at 14°.82, calculated from the equation, gave 331.1, as against 331.0 observed.

μ_∞ *for the Sodium Salts of the Organic Acids.*—Ostwald[1] obtained μ_∞ for the sodium salt of the organic acids by calculating the difference between the conductivity of sodium chloride at a certain dilution, *e.* g., $V = 32$, and at infinite dilution. This difference he assumed to be constant for all sodium salts, and, therefore, by adding it to the conductivity of the sodium salt of any acid at the dilution $V = 32$, μ_∞ for that acid would be obtained. Instead of using this method in this investigation, μ_∞ for the sodium salts was determined directly from conductivity measurements, which are given in the following tables:

Sodium Acetate.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
1024	43.35	62.10	84.82	104.9
2048	44.56	63.83	87.69	107.9
4096	44.60	63.92	87.64	106.8

$$\mu_\infty = 44.56 + 1.520t + 0.00822t^2.$$

Sodium Propionate.

V.	μ_v 0°.	μ_v 13°.57.	μ_v 25°.	μ_v 35°.
1024	39.82	59.63	78.60	96.86
2048	40.57	60.99	81.00	100.6
4096	40.58	60.91	81.03	100.8

$$\mu_\infty = 40.57 + 1.378t + 0.00959t^2.$$

Sodium Butyrate.

V.	μ_v 0°.	μ_v 13°.07.	μ_v 25°.	μ_v 35°.
1024	39.33	58.11	77.69	96.39
2048	40.51	60.29	80.95	100.2
4096	40.54	60.20	80.86	100.1

$$\mu_\infty = 40.51 + 1.401t + 0.00868t^2.$$

[1] Z. physik. Chem., 2, 840 (1888).

Sodium Hippurate.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
1024	35.65	51.30	70.77	86.74
2048	36.23	52.07	71.54	87.98
4096	36.31	52.00	71.60	88.20

$\mu_\infty = 36.23 + 1.250t + 0.00651t^2$.

Sodium Salts of the Toluic Acids.

	μ_v 0°.				μ_v 12°.			
V.	Ortho.	Meta.	Para.	α.	Ortho.	Meta.	Para.	α.
1024	37.82	38.02	38.02	37.89	54.45	54.49	54.41	54.42
2048	38.26	38.25	38.25	38.26	55.05	55.00	55.23	54.87
4096	38.18	38.28	38.28	38.27	54.99	55.09	55.43	54.80

	μ_v 25°.				μ_v 35°.			
V.	Ortho.	Meta.	Para.	α.	Ortho.	Meta.	Para.	α.
1024	74.04	74.33	74.90	73.90	91.87	92.16	91.93	91.98
2048	70.48	75.63	75.44	75.46	92.68	92.88	92.40	92.70
4096	74.92	75.59	75.28	75.11	92.58	92.79	92.29	92.29

μ_∞ (α acid) $= 38.26 + 1.320t + 0.00674t^2$.

Sodium Cinnamate.

V.	μ_v 0°.	μ_v 13°.07.	μ 25°.	μ_v 35°.
1024	27.15	54.59	72.86	89.91
2048	37.69	55.60	74.49	92.06
4096	37.60	55.78	74.41	91.95

$\mu_\infty = 37.69 + 1.271t + 0.00811t^2$.

Sodium Salicylate.

V.	μ_v 0°.	μ_v 12°.32.	μ_v 25 .	μ_v 35 .
1024	40.02	57.77	78.09	96.21
2048	40.55	58.58	79.97	98.90
4096	40.56	58.57	80.00	98.90

$\mu_\infty = 40.51 + 1.353t + 0.00902t^2$.

Sodium Sulphanilate.

V.	μ_v 0°.	μ_v 13°.90.	μ_v 25°.	μ_v 35°.
1024	38.47	55.37	76.20	93.81
2048	39.52	56.28	77.69	96.05
4096	39.36	56.34	77.70	95.85

$\mu_\infty = 39.52 + 1.307t + 0.00879t^2$.

Since, as shown by these results, the above salts give maximum conductivities at $V = 2048$, the remaining salts were measured only at this dilution.

Sodium Mandelate.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
2048	38.25	55.00	76.00	93.20

$\mu_\infty = 38.25 + 1.296t + 0.00856t^2$.

Sodium Crotonate.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
2048	39.53	57.25	79.00	97.03

$\mu_\infty = 39.53 + 1.416t + 0.00639t^2$.

Sodium Pyromucate.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
2048	40.89	59.30	81.84	100.5

$\mu_\infty = 40.89 + 1.478t + 0.00639t^2$.

Sodium Benzoate (solution of dry salt).

V.	μ_v 0°.	μ_v 14°.54.	μ_v 25°.	μ_v 35°.
2048	38.93	60.25	77.69	96.04

$\mu_\infty = 38.93 + 1.348t + 0.00811t^2$.

Sodium Benzoate (by titration).

V.	μ_v 0°.	μ_v 14°.54.	μ_v 25°.	μ_v 35°.
2048	38.91	60.33	77.73	96.25

Sodium Gallate.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
2048	37.91	54.50	74.38	91.80

$\mu_\infty = 37.91 + 1.259t + 0.00799t^2$.

Sodium o-Aminobenzoate.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
2048	38.20	54.81	75.26	92.51

$\mu_\infty = 38.20 + 1.308t + 0.00696t^2$.

Solutions of those sodium salts obtainable from Kahlbaum were made up by weighing out the dry, *purified salt*, while the remainder were prepared by titrating a solution of the free organic acid with a solution of caustic soda. That this alkali contained no appreciable amount of carbonate was proved by comparing the conductivity of solutions of sodium benzoate made by the two methods. From the above results, it is seen that the titration method is sufficiently accurate.

μ_∞ for the sodium salts of all the toluic acids was deter-

mined in order to find out whether there is any difference in the migration velocities of isomeric ions. As there is no difference within the experimental error, the limiting conductivity for isomeric acids can be obtained from measurements on the sodium salt of any one of them. As μ_∞ for the sodium salts of the dibasic acids cannot be experimentally determined, Ostwald's method for calculating this quantity was made use of. If the limiting conductivities of the sodium salts of the monobasic acids are plotted as ordinates against the number of the atoms in the molecule as abscissae, a fairly regular curve is obtained. From this curve μ_∞ for the sodium salts of the dibasic acids may be read off. Even if the value calculated contains an appreciable error, the percentage error introduced into μ_∞ of the organic acid itself will be much less.

The limiting conductivities of many of the organic acids worked with are given below, μ_∞ for the dibasic acids being obtained as described in the preceding paragraph.

Limiting Conductivities.

Acid.	μ_∞ 0°.	μ_∞	μ_∞ 25°.	μ_∞ 35°.
Acetic	227	292 (12°)	361	412
Propionic	223	260 (6°.9)	354	405
Butyric	223	273 (9°.4)	354	404
Toluic	221	284 (12°.0)	349	397
Mandelic	221	283 (12°.0)	349	397
Hippuric	219	280 (12°.0)	345	392
Malonic	223	250 (4°.9)	355	405
Maleic	223	289 (12°.0)	353	402
Crotonic	222	286 (12°.0)	352	402
Racemic	222	286 (12°.0)	350	398
Pyrotartaric	221	290 (12°.0)	349	397
Citric	219	311 (18°.1)	345	392
Pyromucic	223	286 (12°.0)	355	405
Benzoic	222	304 (15°.8)	351	400
Phthalic	221	267 (8°.23)	349	397
Cinnamic	220	248 (5°.3)	348	396
Hydroxybenzoic	223	260 (6°.9)	353	403
Gallic	220	254 (6°.5)	348	396
Sulphanilic	222	255 (6°.3)	351	400
Aminobenzoic	221	260 (7°.5)	349	396

Results.—The results are tabulated in the following pages, molecular conductivities (μ_v) being expressed in Siemen's units. The temperature coefficients expressed in conductivity units and percentages need no explanation.

Table I.—Acetic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 9°.2.	μ_v 25°.	μ_v 35°.
2	1.270	1.560	2.089	2.359
8	2.656	3.292	4.342	4.948
32	5.328	6.612	8.699	9.912
128	10.48	13.04	17.11	19.46
512	20.45	25.40	33.24	37.75
1024	28.03	34.95	45.87	52.09
2048	39.05	48.65	63.00	70.89

Temperature Coefficients.

	0°–9°.2.		9°.2–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.49	0.03	2.15	0.03	1.30
8	0.07	2.61	0.07	2.02	0.06	1.40
32	0.14	2.62	0.13	2.00	0.12	1.39
128	0.28	2.66	0.26	1.98	0.24	1.37
512	0.54	2.63	0.50	1.96	0.45	1.36
1024	0.72	2.57	0.69	1.95	0.62	1.32
2048	1.04	2.67	0.91	1.87	0.79	1.25

Percentage Dissociation.

V.	α 0°.	α 9°.2.	α 25°.	α 35°.
2	0.56	0.56	0.58	0.57
8	1.18	1.19	1.20	1.20
32	2.37	2.40	2.41	2.41
128	4.62	4.71	4.74	4.72
512	8.80	9.13	9.21	9.16
1024	12.35	12.51	12.71	12.64
2048	17.20	17.56	17.45	17.21

Dissociation Constants $\times 10^4$.

V.	0°.	9°.2.	25°.	35°.
2	0.157	0.159	0.169	0.165
8	0.175	0.179	0.183	0.182
32	0.179	0.184	0.186	0.185
128	0.175	0.182	0.184	0.183
512	0.166	0.179	0.182	0.181
1024	0.170	0.175	0.181	0.179
2048	0.174	0.179	0.180	0.175

Table II.—Propionic Acid.

Molecular Conductivity.

V.	μ_v 0°.	μ_v 6°.9.	μ_v 25°.	μ_v 35°.
2	1.030	1.217	1.700	1.913
8	2.291	2.700	3.704	4.207
32	4.631	5.450	7.436	8.422
128	9.004	10.60	14.57	16.50
512	17.47	20.59	28.40	32.14
1024	23.82	28.03	38.94	44.06
2048	32.43	39.24	53.47	60.28

Temperature Coefficients.

	0°–6°.9.		6°.9–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.63	0.03	2.19	0.02	1.25
8	0.06	2.59	0.06	2.05	0.05	1.36
32	0.12	2.56	0.11	2.01	0.10	1.33
128	0.23	2.58	0.22	2.07	0.19	1.32
512	0.45	2.59	0.43	2.10	0.37	1.32
1024	0.61	2.56	0.59	2.11	0.51	1.31
2048	0.84	2.52	0.79	2.01	0.68	1.27

Percentage Dissociation.

V.	α 0°.	α 6°.9.	α 25°.	α 35°.
2	0.46	0.47	0.48	0.47
8	1.03	1.04	1.05	1.04
32	2.08	2.10	2.10	2.08
128	4.04	4.08	4.12	4.07
512	7.83	7.92	8.02	7.93
1024	10.69	10.78	11.00	10.87
2048	14.99	15.09	15.10	14.88

Dissociation Constants $\times 10^4$.

V.	0°.	6°.9	25°.	35°.
2	0.107	0.111	0.116	0.112
8	0.133	0.136	0.138	0.137
32	0.138	0.140	0.141	0.138
128	0.133	0.135	0.138	0.135
512	0.130	0.133	0.137	0.134
1024	0.125	0.127	0.123	0.130
2048	0.129	0.131	0.131	0.127

Table III.—n-Butyric Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 9°.4.	μ_v 25°.	μ_v 35°.
2	1.090	1.341	1.730	1.930
8	2.501	3.062	3.891	4.351
32	5.072	6.230	7.902	8.801
128	10.00	12.23	15.45	17.14
512	19.44	23.79	29.86	33.00
1024	26.82	32.83	41.22	45.26
2048	37.37	45.63	89.20	62.71

Temperature Coefficients.

	0°–9°.4.		9°.4–25°.		25°–35.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.08	2.44	0.03	1.87	0.02	1.16
8	0.06	2.38	0.05	1.74	0.05	1.19
32	0.12	2.43	0.11	1.72	0.09	1.14
128	0.24	2.44	0.21	0.69	0.17	1.09
512	0.46	2.38	0.39	1.64	0.31	1.05
1024	0.64	2.38	0.54	1.64	0.40	0.98
2048	0.88	2.35	0.74	1.61	0.55	0.96

Percentage Dissociation.

V.	α 0°.	α 9°.4.	α 25°.	α 35°.
2	0.49	0.49	0.49	0.48
8	1.12	1.12	1.10	1.08
32	2.27	2.28	2.23	2.18
128	4.48	4.48	4.36	4.24
512	8.72	8.71	8.44	8.17
1024	12.02	12.02	11.64	11.20
2048	16.76	16.71	16.15	15.52

Dissociation Constants $\times 10^4$.

V.	0°.	9°.4.	25°.	35°.
2	0.120	0.120	0.120	0.115
8	0.159	0.159	0.153	0.147
32	0.165	0.166	0.157	0.152
128	0.164	0.164	0.152	0.147
512	0.163	0.163	0.152	0.142
1024	0.161	0.161	0.150	0.138
2048	0.165	0.164	0.152	0.139

Table IV.—Isobutyric Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 16°.46.	μ_v 25°.	μ_v 35°.
2	1.034	1.450	1.633	1.841
8	2.453	3.412	3.821	4.272
32	4.912	6.809	7.621	8.514
128	9.736	13.48	15.13	16.90
512	18.91	26.01	29.30	32.70
1024	26.32	36.18	40.90	45.54
2048	35.96	49.22	55.01	61.35

Temperature Coefficients.

	0°–16°.46.		16°.46–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.45	0.02	1.48	0.02	1.27
8	0.06	2.38	0.05	1.40	0.05	1.18
32	0.12	2.35	0.10	1.40	0.09	1.17
128	0.23	2.33	0.19	1.43	0.18	1.17
512	0.43	2.28	0.36	1.41	0.34	1.16
1024	0.60	2.28	0.51	1.41	0.46	1.13
2048	0.81	2.24	0.68	1.38	0.63	1.15

Percentage Dissociation.

V.	α 0°.	α 16°.46.	α 25°.	α 35°.
2	0.47	0.47	0.46	0.46
8	1.10	1.10	1.08	1.06
32	2.20	2.20	2.15	2.11
128	4.37	4.35	4.27	4.18
512	8.48	8.39	8.28	8.09
1024	11.80	11.67	11.55	11.27
2048	16.13	15.88	15.54	15.19

Dissociation Constants $\times 10^4$.

V.	0°.	16°.46.	25°.	35°.
2	0.108	0.110	0.108	0.108
8	0.153	0.153	0.147	0.141
32	0.155	0.154	0.148	0.142
128	0.156	0.154	0.149	0.143
512	0.154	0.150	0.146	0.139
1024	0.154	0.150	0.147	0.140
2048	0.151	0.146	0.140	0.133

Table V.—Phenylacetic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 13°.25.	μ_v 25°.	μ_v 35°.
32	9.001	11.76	14.15	15.90
128	17.82	23.39	27.96	31.26
512	33.35	43.51	52.39	58.55
1024	45.68	59.59	71.63	79.84
2048	61.00	79.49	95.50	106.3

Temperature Coefficients.

	0°–13°.25.		13°.25–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.21	2.32	0.20	1.73	0.18	1.23
128	0.41	2.32	0.40	1.70	0.33	1.18
512	0.77	2.30	0.76	1.72	0.62	1.18
1024	1.05	2.30	1.03	1.72	0.82	1.15
2048	1.40	2.29	1.36	1.71	1.06	1.13

Percentage Dissociation.

V.	α 0°.	α 13°.25.	α 25°.	α 35°.
32	4.07	4.06	4.05	4.01
128	8.06	8.06	8.01	7.87
512	15.09	15.01	14.97	14.75
1024	20.67	20.55	20.52	20.11
2048	27.60	27.41	27.36	26.77

Dissociation Constants $\times 10^4$.

V.	0°.	13°.25.	25°.	35°.
32	0.540	0.536	0.536	0.522
128	0.552	0.553	0.545	0.526
512	0.524	0.518	0.515	0.499
1024	0.526	0.519	0.518	0.494
2048	0.514	0.507	0.504	0.478

Table VI.—Mandelic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
8	12.60	16.10	19.86	22.45
32	24.49	31.21	38.56	43.62
128	46.40	59.64	72.96	82.39
512	82.21	106.1	129.6	146.2
1024	106.0	135.2	167.4	188.7
2048	132.4	168.3	205.5	234.5

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.29	2.32	0.29	1.80	0.26	1.30
32	0.56	2.29	0.56	1.81	0.51	1.31
128	1.10	2.38	1.02	1.72	0.94	1.29
512	1.99	2.42	1.81	1.71	1.66	1.28
1024	2.43	2.30	2.48	1.83	2.13	1.27
2048	2.99	2.26	2.86	1.70	2.90	1.40

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
8	5.70	5.69	5.69	5.65
32	11.09	11.03	11.05	10.98
128	20.99	20.78	20.90	20.75
512	37.20	36.98	37.15	36.84
1024	47.96	47.76	47.97	47.53
2048	59.91	59.47	59.03	59.06

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
8	4.32	4.29	4.29	4.24
32	4.30	4.27	4.29	4.24
128	4.36	4.26	4.31	4.25
512	4.30	4.24	4.30	4.20
1024	4.32	4.26	4.32	4.21
2048	4.37	4.26	4.16	4.16

Table VII.—Hippuric Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ 35°.
128	33.96	44.42	55.17	62.15
512	61.66	80.54	100.2	113.5
1024	81.10	105.8	131.1	147.2
2048	103.0	134.1	165.8	185.9

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
128	0.87	2.57	0.83	1.86	0.70	1.27
512	1.57	2.55	1.52	1.84	1.25	1.25
1024	2.06	2.54	1.95	1.84	1.61	1.23
2048	2.59	2.52	2.44	1.82	2.01	1.21

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
128	15.51	15.86	15.99	15.85
512	28.16	28.76	29.04	28.96
1024	37.03	37.79	38.00	37.55
2048	47.03	47.88	48.06	47.42

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
128	2.22	2.34	2.38	2.33
512	2.16	2.27	2.32	2.31
1024	2.13	2.24	2.28	2.26
2048	2.04	2.15	2.17	2.09

Table VIII.—Malonic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 4°.9.	μ_v 25°.	μ_v 35°.
2	11.81	13.34	19.61	22.51
8	23.19	26.20	38.40	44.03
32	43.51	49.25	72.23	82.55
128	78.30	88.83	129.8	148.2
512	127.1	143.4	208.7	237.4
1024	153.3	173.2	251.2	284.8
2048	176.9	199.1	289.1	327.6

Temperature Coefficients.

	0°–4°.9.		4°.9–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.31	2.64	0.31	2.34	0.29	1.48
8	0.61	2.66	0.61	2.32	0.58	1.47
32	1.17	2.69	1.14	2.32	1.03	1.43
128	2.09	2.67	2.04	2.30	1.84	1.42
512	3.33	2.62	3.25	2.27	2.87	1.38
1024	4.06	2.65	3.88	2.24	3.36	1.34
2048	4.53	2.56	4.48	2.25	3.75	1.30

Percentage Dissociation.

V.	α 0°.	α 4°.9.	α 25°.	α 35°.
2	5.30	5.34	5.53	5.55
8	10.40	10.48	10.81	10.87
32	19.57	19.70	20.34	20.38
128	35.12	35.53	36.58	36.59
512	56.99	57.36	58.80	58.60
1024	68.74	69.28	70.76	70.31
2048	79.32	79.66	81.45	80.89

Dissociation Constants $\times 10^4$.

V.	0°.	4°.9.	25°.	35°.
2	14.8	15.0	16.1	16.4
8	15.1	15.3	16.4	16.5
32	14.8	15.1	16.3	16.3
128	14.8	15.3	16.4	16.5
512	14.8	15.1	16.4	16.2
1024	14.8	15.3	16.7	16.3
2048	14.9	15.3	17.5	16.8

Table IX.—Succinic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 5°.7.	μ_v 25°.	μ_v 35°.
8	4.570	5.371	8.032	9.251
32	9.211	10.72	16.01	18.36
128	18.24	21.35	31.24	35.80
512	34.75	40.59	59.34	67.87
1024	47.89	55.91	81.31	92.89
2048	64.61	75.29	109.6	124.8

Temperature Coefficients.

	0°–5°.7.		5°.7–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent
8	0.14	3.07	0.14	2.57	0.12	1.52
32	0.28	3.03	0.27	2.56	0.24	1.47
128	0.55	2.99	0.51	2.40	0.46	1.46
512	1.02	2.95	0.97	2.39	0.85	1.44
1024	1.41	2.94	1.32	2.36	1.16	1.42
2048	1.87	2.90	1.78	2.36	1.52	1.39

Percentage Dissociation.

V.	α 0°.	α 5°.7.	α 25°.	α 35°.
8	2.05	2.15	2.26	2.28
32	4.13	4.29	4.51	4.53
128	8.18	8.54	8.80	8.84
512	15.58	16.24	16.72	16.76
1024	20.47	22.37	22.91	22.91
2048	28.97	30.11	30.88	30.81

Dissociation Constants $\times 10^4$.

V.	0°.	5°.7.	25°.	35°.
8	0.537	0.590	0.655	0.667
32	0.556	0.600	0.666	0.673
128	0.569	0.623	0.664	0.670
512	0.562	0.615	0.655	0.659
1024	0.572	0.629	0.665	0.665
2048	0.577	0.634	0.675	0.670

Table X.—Maleic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
32	108.1	141.0	175.4	198.8
128	159.2	206.6	256.2	290.7
512	198.5	257.4	317.6	360.8
1024	212.8	274.7	337.9	384.6
2048	221.1	286.6	352.3	400.8

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	2.74	2.54	2.65	1.88	2.34	1.34
128	3.95	2.48	3.82	1.85	3.45	1.35
512	4.85	2.50	4.63	1.80	4.32	1.36
1024	5.14	2.43	4.86	1.77	4.67	1.38
2048	5.46	2.47	5.05	1.76	4.85	1.41

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
32	48.48	48.78	49.72	49.46
128	71.50	71.50	72.56	72.31
512	89.00	89.06	89.97	89.76
1024	95.06	95.06	95.72	95.68
2048	99.10	99.17	99.79	99.72

Dissociation Constants $\times$ 10^4.

V.	α 0°.	α 12°.	α 25°.	α 35°.
32	143.0	145.0	154.0	151.0
128	141.0	140.0	150.0	148.0
512	141.0	142.0	158.0	154.0
1024	179.0	179.0	209.0	208.0
2048	...	...	...	...

Table XI.—Fumaric Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
32	35.46	46.66	58.00	65.79
128	65.67	86.42	107.2	121.2
512	114.1	149.1	184.9	209.6
1024	141.4	184.9	228.1	258.1
2048	176.5	229.0	281.0	318.1

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.94	2.64	0.87	1.87	1.78	1.19
128	1.73	2.63	1.60	1.85	1.46	1.20
512	2.92	2.56	2.75	1.85	2.47	1.18
1024	3.62	2.56	3.32	1.80	3.00	1.17
2048	4.33	2.45	4.00	1.75	3.71	1.17

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
32	15.90	16.14	16.43	16.37
128	29.45	29.90	30.37	30.15
512	51.17	51.59	52.37	52.14
1024	63.43	63.97	64.62	64.21
2048	79.14	79.23	79.60	79.12

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
32	9.40	9.72	10.1	10.0
128	9.61	9.97	10.4	10.2
512	10.5	10.7	11.3	11.0
1024	10.7	11.1	11.5	11.2
2048	14.7	14.8	15.2	14.6

Table XII.—Citraconic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
32	68.66	85.82	103.0	115.1
128	114.3	144.0	173.4	194.4
512	165.9	210.2	255.4	288.2
1024	186.1	237.0	289.1	226.5
2048	200.5	257.1	315.0	356.0

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	1.43	2.08	1.32	1.54	1.21	1.18
128	2.48	2.17	2.26	1.57	2.10	1.21
512	3.69	2.23	3.48	1.65	3.28	1.28
1024	4.24	2.28	4.00	1.69	3.74	1.29
2048	4.70	2.34	4.46	1.74	4.10	1.30

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
32	31.02	30.16	29.34	28.77
128	51.64	50.60	49.40	48.60
512	74.98	73.86	72.76	72.04
1024	84.09	83.28	82.37	81.62
2048	90.59	90.31	89.74	89.01

Dissociation Constants $\times$ 10^4.

V.	0°.	12°.	25°.	35°.
32	43.6	40.7	38.1	36.3
128	43.1	40.5	37.7	35.9
512	43.9	40.8	38.0	36.2
1024	43.4	40.5	37.6	35.4
2048	42.6	41.0	38.3	35.3

Table XIII.—Mesaconic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
32	33.31	42.85	52.00	58.04
128	62.60	80.18	97.30	108.5
512	108.0	139.0	168.5	188.2
1024	134.7	172.9	209.8	234.0
2048	160.9	206.3	250.0	278.8

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.80	2.39	0.70	1.63	0.60	1.16
128	1.47	2.36	1.32	1.64	1.12	1.15
512	2.54	2.35	2.27	1.63	1.97	1.16
1024	3.78	2.37	2.84	1.64	2.42	1.15
2048	4.09	2.35	3.36	1.63	2.88	1.15

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
32	15.05	15.04	14.81	14.51
128	28.29	28.17	27.72	27.13
512	48.79	48.67	48.00	47.06
1024	60.87	60.74	59.77	58.49
2048	72.69	72.49	71.22	69.69

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
32	8.4	8.4	8.1	7.7
128	8.7	8.6	8.3	7.9
512	9.1	9.0	8.6	8.2
1024	9.3	9.2	8.7	8.1
2048	9.5	9.3	8.6	9.8

Table XIV.—Itaconic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 18°.12.	μ_v 25°.	μ_v 35°.
32	13.50	20.77	23.68	27.22
128	26.00	39.95	45.52	52.21
512	49.51	74.57	84.74	97.11
1024	66.70	99.51	113.3	129.8
2048	87.91	129.9	147.3	167.5

Temperature Coefficients.

	0°–18°.12.		18°.12–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.40	2.97	0.42	2.04	0.35	1.50
128	0.77	2.97	0.83	2.03	0.67	1.47
512	1.38	2.79	1.48	1.98	1.24	1.46
1024	1.81	2.71	2.01	2.01	1.65	1.45
2048	2.32	2.64	2.53	1.95	2.02	1.44

Percentage Dissociation.

V.	α 0°.	α 18°.12.	α 25°.	α 35°.
32	6.10	6.57	6.75	6.80
128	11.75	12.64	12.97	13.05
512	22.38	23.60	24.15	24.28
1024	30.14	31.49	32.28	32.45
2048	39.72	41.11	41.98	41.87

Dissociation Constants $\times$ 10^4.

V.	0°.	18°.12.	25°.	35°.
32	1.24	1.45	1.53	1.55
128	1.23	1.43	1.51	1.53
512	1.26	1.43	1.50	1.52
1024	1.27	1.42	1.50	1.52
2048	1.28	1.40	1.49	1.47

Table XV.—Crotonic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
8	2.752	3.640	4.550	5.177
32	5.526	7.312	9.123	10.31
128	10.92	14.49	18.00	20.29
512	21.25	28.23	35.15	39.85
1024	29.14	38.50	48.04	54.60
2048	39.78	53.41	65.33	74.19

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.07	2.69	0.07	1.92	0.06	1.38
32	0.15	2.69	0.14	1.91	0.12	1.31
128	0.30	2.72	0.27	1.86	0.23	1.27
512	0.58	2.74	0.53	1.89	0.47	1.34
1024	0.78	2.68	0.73	1.91	0.66	1.37
2048	1.05	2.67	0.99	1.90	0.89	1.36

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
8	1.24	1.27	1.29	1.29
32	2.49	2.56	2.59	2.57
128	4.92	5.07	5.11	5.05
512	9.57	9.87	10.00	9.91
1024	13.12	13.46	13.65	13.58
2048	17.74	18.32	18.57	18.45

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
8	0.195	0.205	0.212	0.211
32	0.199	0.210	0.215	0.211
128	0.199	0.211	0.215	0.210
512	0.198	0.211	0.216	0.213
1024	0.194	0.205	0.211	0.208
2048	0.187	0.201	0.207	0.204

Table XVI.—Racemic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
8	18.02	24.35	30.97	35.98
32	34.60	46.85	59.65	69.03
128	63.24	85.15	108.2	124.7
512	110.6	147.8	187.0	215.1
1024	139.0	183.7	230.0	264.3
2048	175.3	231.5	290.4	333.8

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	1.53	2.93	0.51	2.09	0.50	1.62
32	1.02	2.93	0.99	2.10	0.95	1.59
128	1.83	2.89	1.77	2.08	1.65	1.53
512	3.10	2.80	3.02	2.04	2.81	1.50
1024	3.73	2.68	3.56	2.94	3.43	1.49
2048	4.68	2.67	4.53	1.95	4.34	1.50

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
8	8.15	8.51	8.85	9.04
32	15.66	16.38	17.04	17.34
128	28.62	29.77	30.91	31.32
512	50.03	51.68	53.42	54.04
1024	62.90	64.22	65.70	66.40
2048	79.30	80.93	82.96	83.85

Dissociation Constants $\times$ 10^4.

V.	0°.	12°.	25°.	35°.
8	9.1	9.9	10.8	11.2
32	9.1	10.0	10.9	11.3
128	9.0	9.9	10.8	11.2
512	9.8	10.8	12.0	12.4
1024	10.44	11.3	12.3	12.8
2048	14.8	16.8	19.7	21.3

Table XVII.—Pyrotartaric Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
8	5.403	7.150	9.045	10.41
32	10.94	14.41	18.13	20.80
128	21.08	27.68	35.00	40.00
512	40.45	53.06	67.02	76.56
1024	54.18	71.31	89.73	102.4
2048	73.00	96.00	120.3	137.7

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.15	2.70	0.15	2.04	0.14	1.49
32	0.29	2.64	0.29	1.99	0.27	1.47
128	0.56	2.61	0.56	2.03	0.50	1.43
512	1.05	2.60	1.07	2.02	0.95	1.42
1024	1.43	2.63	1.42	1.99	1.27	1.42
2048	1.92	2.62	1.87	1.95	1.74	1.45

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
8	2.44	2.46	2.59	2.62
32	4.95	4.97	5.20	5.24
128	9.54	9.55	10.03	10.08
512	18.30	18.30	19.21	19.29
1024	24.51	24.60	25.71	25.79
2048	33.03	33.11	34.46	34.69

Dissociation Constants $\times$ 10^4.

V.	0°.	12°.	25°.	35°.
8	77	78	86	89
32	81	81	89	90
128	79	79	87	88
512	80	80	89	90
1024	78	78	87	88
2048	80	80	88	90

Table XVIII.—Citric Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 18°.10.	μ_v 25.	μ_v 35°.
8	15.64	24.34	27.50	32.05
32	30.27	46.74	52.76	61.42
128	55.94	86.40	97.30	112.7
512	97.22	148.3	167.6	195.1
1024	127.3	193.3	218.1	251.9
2048	153.2	229.3	257.9	297.8

Temperature Coefficients.

	0°–18°.10.		18°.10–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.48	3.07	0.46	1.88	0.46	1.66
32	0.91	3.00	0.87	1.87	0.87	1.64
128	1.68	3.01	1.58	1.83	1.54	1.58
512	2.82	2.90	2.80	1.87	2.66	1.58
1024	3.64	2.86	3.59	1.86	3.38	1.55
2048	4.20	2.75	4.15	1.81	3.99	1.55

Percentage Dissociation.

V.	α 0°.	α 18°.10.	α 25°.	α 35°.
8	7.14	7.82	7.97	8.18
32	13.82	15.03	15.30	15.67
128	25.55	27.77	28.20	28.74
512	44.40	47.46	48.59	49.76
1024	58.13	62.16	63.23	64.25
2048	69.97	73.72	74.74	75.98

Dissociation Constants $\times$ 10^4.

V.	0°.	18°.10.	25°.	35°.
8	6.87	8.30	8.63	9.10
32	6.92	8.30	8.63	9.10
128	6.85	8.34	8.66	9.05
512	6.92	8.38	8.97	9.63
1024	7.88	9.96	10.6	11.3
2048	7.96	10.1	10.8	11.7

Table XIX.—Pyromucic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
8	17.47	22.01	26.29	28.94
32	34.24	42.76	51.15	56.37
128	62.90	79.22	94.61	104.5
512	107.1	136.4	163.2	108.0
1024	132.0	169.0	201.3	222.9
2048	159.5	203.0	245.1	270.1

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.38	2.18	0.33	1.50	0.28	1.05
32	0.71	2.08	0.65	1.61	0.52	1.04
128	1.36	2.16	1.18	1.50	0.99	1.05
512	2.44	2.28	2.06	1.51	1.68	1.03
1024	3.08	2.31	2.49	1.47	2.06	1.02
2048	3.62	2.27	3.24	1.59	2.50	1.02

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
8	7.83	7.64	7.38	7.15
32	15.36	14.85	14.41	13.92
128	28.21	27.51	26.65	25.80
512	48.03	47.36	45.97	44.44
1024	59.20	58.68	56.99	55.03
2048	71.53	70.49	69.05	66.70

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
8	8.3	7.9	7.4	6.9
32	8.7	8.1	7.6	7.0
128	8.7	8.1	7.6	7.0
512	8.7	8.3	7.6	6.9
1024	8.4	8.1	7.4	6.6
2048	8.7	8.2	7.5	6.5

Table XX.—Benzoic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 15°.80.	μ_v 25°.	μ_v 35°.
64	13.42	19.08	22.29	25.40
128	18.49	26.93	31.39	35.71
512	36.00	51.30	59.79	67.81
1024	47.63	68.33	79.56	90.11
2048	64.95	91.30	106.0	119.7

Temperature Coefficients.

	0°–15°.80°.		15°.80–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.36	2.67	0.35	1.83	0.31	1.40
128	0.50	2.66	0.49	1.81	0.43	1.38
512	0.97	2.64	0.92	1.81	0.80	1.35
1024	1.26	2.64	1.22	1.79	1.06	1.33
2048	1.67	2.57	1.60	1.75	1.37	1.30

Percentage Dissociation.

V.	α 0°.	α 13°.80.	α 25°.	α 35°.
64	6.04	6.32	6.35	6.34
128	8.46	8.92	8.94	8.92
512	16.21	17.00	17.02	16.94
1024	21.45	22.62	22.67	22.52
2048	29.25	30.24	30.20	29.92

Dissociation Constants $\times$ 10^4.

V.	0°.	15°.80	25°.	35°.
64	0.607	0.666	0.672	0.672
128	0.611	0.682	0.686	0.684
512	0.613	0.679	0.683	0.676
1024	0.572	0.646	0.649	0.640
2048	0.591	0.640	0.638	0.624

Table XXI.—o-Toluic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
512	54.71	68.32	81.09	88.44
1024	71.65	89.87	106.7	116.7
2048	95.06	118.7	141.0	154.7

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	1.13	2.07	0.98	1.44	0.74	0.91
1024	1.52	2.11	1.29	1.44	1.00	0.94
2048	1.93	2.03	1.72	1.44	1.33	0.94

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
512	24.76	24.11	23.23	22.20
1024	32.44	31.71	30.50	29.47
2048	43.01	41.75	40.54	39.16

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
512	1.59	1.49	1.37	1.25
1024	1.52	1.44	1.32	1.30
2048	1.59	1.46	1.35	1.22

Table XXII.—m-*Toluic Acid. Molecular Conductivity.*

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
512	33.05	43.57	54.60	62.05
1024	45.20	59.43	74.16	83.93
2048	61.24	80.79	100.4	113.1

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	0.88	2.65	0.85	1.95	0.75	1.37
1024	1.19	2.62	1.13	1.91	0.98	1.32
2048	1.63	2.66	1.51	1.87	1.27	1.27

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
512	14.95	15.44	15.64	15.63
1024	20.45	21.05	21.25	21.14
2048	27.71	28.63	28.77	28.49

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
512	0.513	0.550	0.567	0.565
1024	0.513	0.548	0.560	0.554
2048	0.519	0.560	0.567	0.554

Table XXIII.—p-*Toluic Acid. Molecular Conductivity.*

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
512	...	...	48.48	55.44
1024	39.63	52.52	66.13	75.54
2048	54.12	71.75	89.96	103.5

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	....	....	....	....	0.70	1.44
1024	1.07	2.76	1.05	1.99	0.94	1.42
2048	1.47	2.72	1.40	1.95	1.35	1.50

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
512	...	...	13.89	13.96
1024	17.93	18.49	18.95	19.02
2048	24.49	25.26	25.78	26.07

Dissociation Constants $\times$ 10^4.

V.	0°.	12°.	25°.	35°.
512	...	...	0.438	0.433
1024	0.383	0.410	0.433	0.437
2048	0.388	0.417	0.437	0.449

Table XXIV.—o-Phthalic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 8°.23.	μ_v 25°.	μ_v 35°.
64	55.98	66.45	85.92	96.48
128	75.56	88.32	114.8	128.9
512	122.3	145.7	189.2	212.5
1024	148.2	177.1	231.9	259.7
2048	174.2	208.4	272.7	306.0

Temperature Coefficients.

	0°–8°.23.		8°.23–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	1.27	2.27	1.16	1.75	1.06	1.23
128	1.67	2.24	1.58	1.79	1.41	1.23
512	2.84	2.33	2.59	1.78	2.33	1.23
1024	3.51	2.37	3.27	1.85	2.78	1.20
2048	4.16	2.39	3.83	1.84	3.33	1.22

Percentage Dissociation.

V.	α 0°.	α 8°.23.	α 25°.	α 35°.
64	25.33	24.89	24.62	24.31
128	33.75	33.09	32.90	32.47
512	55.34	54.58	54.23	53.52
1024	67.07	66.33	66.45	65.42
2048	78.81	78.05	78.14	77.07

Dissociation Constants $\times$ 10^4.

V.	0°.	8°.23.	25°.	35°.
64	13.4	12.9	12.6	12.2
128	13.4	12.8	12.6	12.2
512	13.4	12.8	12.5	12.0
1024	13.4	12.8	12.8	12.1
2048	14.3	13.6	13.6	12:7

Table XXV.—Cinnamic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 5°.3.	μ_v 25°.	μ_v 35°.
512	26.50	30.67	44.60	50.70
1024	36.40	42.11	61.22	69.63
2048	49.69	57.40	83.45	94.81

Temperature Coefficients.

	0°–5°.3.		5°.3–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	0.79	2.97	0.71	2.31	0.61	1.37
1024	1.08	2.96	0.97	2.30	0.84	1.37
2048	1.46	2.93	1.32	2.30	1.14	1.36

Percentage Dissociation.

V.	α 0°.	α 5°.3.	α 25°.	α 35°.
512	12.04	12.37	12.81	12.80
1024	16.55	16.97	17.59	17.58
2048	22.08	23.14	23.98	23.94

Dissociation Constants $\times 10^4$.

V.	0°.	5°.3	25°.	35°.
512	0.322	0.341	0.368	0.367
1024	0.320	0.339	0.367	0.366
2048	0.305	0.342	0.370	0.368

Table XXVI.—Salicylic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 6°.9.	μ_v 25°.	μ_v 35°.
64	...	...	80.50	92.80
128	62.65	75.59	108.3	125.1
512	105.4	126.4	181.2	207.0
1024	130.7	156.9	223.2	255.4
2048	153.8	183.9	259.9	295.7

Temperature Coefficients.

	0°–6°.9.		6°.9–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	....	....	....	....	1.23	1.53
128	1.88	2.99	1.83	2.42	1.68	1.55
512	3.12	2.96	3.00	2.37	2.58	1.42
1024	3.80	2.91	3.63	2.31	3.22	1.41
2048	4.36	2.84	2.16	2.26	3.58	1.38

Percentage Dissociation.

V.	α 0°.	α 6°.9.	α 25°.	α 35°.
64	...	...	22.80	23.02
128	28.09	29.06	30.68	31.03
512	47.28	48.62	51.34	51.37
1024	58.60	60.34	63.22	63.37
2048	68.96	70.73	73.62	73.36

Dissociation Constants $\times 10^4$.

V.	0°.	6°.9.	25°.	35°.
64	...	...	10.5	10.7
128	8.6	9.3	10.6	10.9
512	8.3	9.0	10.6	10.6
1024	8.1	9.0	10.6	10.7
2048	7.5	8.4	9.4	9.9

Table XXVII.—m-*Hydroxybenzoic Acid. Molecular Conductivity.*

V.	μ_v 0°.	μ_v 13°.22.	μ_v 25°.	μ_v 35°.
64	14.65	19.97	24.35	27.74
128	20.48	27.85	33.95	38.63
512	39.04	52.89	64.50	73.28
1024	53.09	72.01	87.80	99.70
2048	71.20	96.03	116.9	132.6

Temperature Coefficients.

	0°–13°.22.		13°.22–25°.		25°–35.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.40	2.75	0.37	1.86	0.34	0.39
128	0.56	2.72	0.52	1.86	0.47	1.38
512	1.05	2.68	0.99	1.86	0.88	1.36
1024	1.44	2.71	1.31	1.81	1.19	1.36
2048	1.94	2.74	1.72	1.78	1.57	1.34

Percentage Dissociation.

V.	α 0°.	α 13°.22.	α 25°.	α 35°.
64	6.57	6.82	6.90	6.88
128	9.18	9.50	9.62	9.58
512	17.51	18.05	18.27	18.19
1024	23.81	24.56	24.87	24.74
2048	31.93	32.77	33.12	32.91

Dissociation Constants $\times$ 10^4.

V.	0°.	13°.22.	25°.	35°.
64	0.722	0.779	0.799	0.795
128	0.725	0.780	0.799	0.794
512	0.725	0.776	0.798	0.798
1024	0.726	0.781	0.804	0.794
2048	0.715	0.780	0.801	0.788

Table XXVIII.—p-*Hydroxybenzoic Acid. Molecular Conductivity.*

V.	μ_v 0°.	μ_v 13°.23.	μ_v 25.°	μ_v 35°.
64	8.746	11.99	14.79	16.97
128	18.29	16.81	20.69	23.71
512	23.87	32.45	39.96	45.77
1024	33.03	44.91	55.30	63.24
2048	44.40	60.39	74.14	85.60

Temperature Coefficients.

	0°–13°.23.		13°.23–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.25	2.80	0.24	1.98	0.22	1.46
128	0.34	2.78	0.33	1.96	0.30	1.46
512	0.65	2.72	0.64	1.97	0.58	1.45
1024	0.90	2.72	0.88	1.97	0.79	1.44
2048	1.21	2.72	1.17	1.94	1.05	1.41

Percentage Dissociation.

V.	α 0°.	α 13°.23.	α 25°.	α 35°.
64	3.92	4.09	4.19	4.21
128	5.51	5.74	5.86	5.88
512	10.70	11.08	11.32	11.36
1024	14.81	15.32	15.66	15.70
2048	19.91	20.61	21.00	21.00

Dissociation Constants $\times$ 10^4.

V.	0°.	13°.23.	25°.	35°.
64	0.250	0.273	0.286	0.289
128	0.251	0.273	0.285	0.287
512	0.251	0.269	0.282	0.284
1024	0.252	0.271	0.284	0.285
2048	0.242	0.261	0.273	0.273

Table XXIX.—Gallic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 6°.5.	μ_v 25°.	μ_v 35°.
64	9.790	11.66	16.90	19.36
128	14.01	16.55	23.60	27.10
512	28.89	34.08	48.33	55.12
1024	37.84	44.63	62.50	71.18
2048	51.50	60.72	85.02	96.7

Temperature Coefficients.

	0°–6°.5.		6°.5–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.29	2.94	0.28	2.43	0.25	1.46
128	0.39	2.79	0.38	2.30	0.35	1.48
512	0.80	2.77	0.77	2.26	0.68	1.41
1024	1.05	2.76	0.97	2.17	0.87	1.39
2048	1.42	2.75	1.31	2.16	1.17	1.38

Percentage Dissociation.

V.	α 0°.	α 6°.5.	α 25°.	α 35°.
64	4.44	4.59	4.86	4.89
128	6.36	6.51	6.78	6.85
512	13.11	13.41	13.89	13.92
1024	17.18	17.55	17.96	17.98
2048	23.37	23.88	24.43	24.43

Dissociation Constants $\times 10^4$.

V.	0°.	6°.5.	25°.	35°.
64	0.323	0.345	0.387	0.393
128	0.338	0.354	0.385	0.394
512	0.387	0.405	0.437	0.440
1024	0.348	0.365	0.384	0.385
2048	0.349	0.366	0.386	0.386

Table XXX.—Metanilic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 12°.	μ_v 25°.	μ_v 35°.
32	11.60	18.01	26.89	35.01
128	22.90	34.84	51.40	66.89
512	42.76	65.66	95.10	121.1
1024	58.01	87.96	125.8	158.1
2048	76.38	115.1	162.8	203.5

Temperature Coefficients.

	0°–12°.		12°–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.53	4.61	0.68	3.79	0.81	3.02
128	1.00	4.40	1.28	3.66	1.55	3.01
512	1.91	4.46	2.27	3.45	2.60	2.73
1024	2.50	2.30	2.91	3.41	3.23	2.63
2048	3.23	4.22	3.67	3.19	4.07	2.50

Percentage Dissociation.

V.	α 0°.	α 12°.	α 25°.	α 35°.
32	5.23	6.32	7.67	8.75
128	10.27	12.23	14.64	16.72
512	19.26	23.04	27.10	30.27
1024	26.13	30.87	25.84	39.53
2048	34.41	40.39	46.37	50.88

Dissociation Constants $\times 10^4$.

V.	0°.	12°.	25°.	35°.
32	0.90	1.33	1.99	2.62
128	0.89	1.33	1.96	2.62
512	0.90	1.35	1.97	2.57
1024	0.90	1.35	1.96	2.52
2048	0.88	1.34	1.96	2.57

Table XXXI.—Sulphanilic Acid. Molecular Conductivity.

V.	μ_v 0°.	μ_v 6°.3.	μ_v 25°.	μ_v 35°.
32	21.80	27.25	47.20	60.0
128	40.66	50.89	87.51	110.2
512	74.25	91.33	152.8	188.3
1024	96.40	118.1	193.0	237.0
2048	121.5	148.4	235.2	281.5

Temperature Coefficients.

	0°–6°.3.		6°.3–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.88	4.03	1.07	3.91	1.28	2.71
128	1.62	3.99	1.96	3.85	2.27	2.59
512	2.71	3.65	3.29	3.60	3.55	2.33
1024	3.45	3.57	4.01	3.39	4.40	2.28
2048	4.27	3.52	4.53	3.06	4.63	1.97

Percentage Dissociation.

V.	α 0°.	α 6°.3	α 25°.	α 35°.
32	9.82	10.69	13.45	15.00
128	18.31	19.96	24.93	27.55
512	33.44	35.82	43.52	47.08
1024	43.42	46.33	54.99	58.75
2048	54.71	58.21	67.02	70.37

Dissociation Constants $\times$ 10^4.

V.	0°.	6°.3.	25°.	35°.
32	3.34	4.00	6.53	8.27
128	3.20	3.89	6.47	8.19
512	3.28	3.90	6.55	8.18
1024	3.26	3.90	6.56	8.17
2048	3.23	3.96	6.64	8.16

Table XXXII.—o-*Aminobenzoic Acid. Molecular Conductivity.*

V.	μ_v 0°.	μ_v 7°.5.	μ_v 25°.	μ_v 35°.
64	3.071	4.172	7.150	9.001
128	4.642	6.283	10.71	13.39
512	10.90	14.31	23.26	28.96
1024	16.03	20.48	33.53	41.57
2048	21.93	28.30	45.26	55.78

Temperature Coefficients.

	0°–7°.5.		7°.5–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.15	4.78	0.17	4.08	0.19	2.59
128	0.21	4.52	0.25	3.98	0.27	2.57
512	0.45	4.17	0.51	3.58	0.57	2.45
1024	0.65	4.03	0.72	3.46	0.81	2.40
2048	0.85	3.87	0.97	3.43	1.05	2.33

Percentage Dissociation.

V.	α 0°.	α 7°.5.	α 25°.	α 35°.
64	1.39	1.60	2.05	2.27
128	2.12	2.42	3.07	3.38
512	4.93	5.50	6.67	7.31
1024	7.25	7.87	9.62	10.48
2048	7.88	10.88	13.00	14.07

Dissociation Constants $\times$ 10^4.

V.	0°.	7°.5.	25°.	35°.
64	0.0306	0.0408	0.0671	0.0824
128	0.0360	0.0467	0.0761	0.0922
512	0.0499	0.0626	0.0932	0.112
1024	0.0554	0.0658	0.100	0.120
2048	0.0329	0.0649	0.0948	0.113

Table XXXIII.—p-*Aminobenzoic Acid. Molecular Conductivity.*

V.	μ_v 0°.	μ_v 10°.19.	μ_v 25°.	μ_v 35°.
64	3.711	5.136	7.370	8.919
128	5.346	7.527	10.84	12.97
512	12.57	17.39	24.54	29.06
1024	18.87	25.71	35.07	41.31
2048	28.32	37.21	50.13	58.56

Temperature Coefficients.

	0°–10°.19.		10°.19–25°.		25°–35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.14	3.78	0.15	2.92	0.16	2.10
128	0.21	4.00	0.22	2.97	0.21	1.96
512	0.47	3.76	0.48	2.78	0.45	1.84
1024	0.67	3.57	0.63	2.46	0.62	1.79
2048	0.87	3.08	0.87	2.35	0.84	1.68

Percentage Dissociation.

V.	α 0°.	α 10°.19.	α 25°.	α 35°.
64	1.68	1.87	2.11	2.25
128	2.42	2.75	3.11	3.27
512	5.69	6.34	7.04	7.47
1024	8.54	9.38	10.07	10.42
2048	13.73	13.28	14.38	14.77

Dissociation Constants $\times$ 10^4.

V.	0°.	10°.19.	25°.	35°.
64	0.0448	0.0559	0.0714	0.0790
128	0.0468	0.0606	0.0780	0.0865
512	0.0670	0.0838	0.104	0.118
1024	0.0678	0.0949	0.110	0.119
2048	0.107	0.104	0.118	0.125

While inorganic salts and mineral acids all behave in the same way with respect to the change in dissociation with the temperature, the organic acids present a perplexing problem, when an attempt is made to deduce any relation between the change in their dissociation and their chemical constitution. With many of the acids a maximum in dissociation occurs between 25° and 35°. This statement applies to the following acids: acetic, propionic, phenylacetic, hippuric, malonic, maleic, fumaric, crotonic, benzoic, *m*-toluic, cinnamic, salicylic, *m*-hydroxybenzoic. The dissociation of succinic, itaconic, racemic, pyrotartaric, citric, *p*-hydroxybenzoic, gallic,

metanilic, sulphanilic, *o*- and *p*-aminobenzoic acids, increases from 0° up to 35° without a maximum, but several give indications that a maximum would appear at a slightly higher temperature. The dissociation of the remaining acids—*n*-butyric and isobutyric, mandelic, citraconic, mesaconic, *o*-toluic, *o*-phthalic—decreases regularly with rise in temperature from 0°. The most probable dissociation constants of all the acids are given in Table XXXIV, from which the above relations become clear:

Table XXXIV.—$K \times 10^4$.

Acid.	0°.	12°.	25°.	35°.
Acetic	0.175	....	0.184	0.183
Propionic	0.133	....	0.138	0.136
n-Butyric	0.163	....	0.153	0.147
Isobutyric	0.155	....	0.148	0.142
Phenylacetic	0.540	....	0.545	0.526
Mandelic	4.30	4.29	4.29	4.24
Hippuric	2.22	2.34	2.38	2.33
Malonic	1.48	....	16.3	16.3
Succinic	0.562	....	0.655	0.659
Maleic	143.0	145.0	154.0	151.0
Fumaric	9.40	9.72	10.1	10.0
Citraconic	43.6	40.7	38.1	36.3
Mesaconic	8.4	8.4	8.1	7.7
Itaconic	1.24	1.45	1.53	1.55
Crotonic	0.199	0.210	0.215	0.211
Racemic	9.1	9.9	10.8	11.2
Pyrotartaric	79.0	79.0	87.0	88.0
Citric	6.85	....	8.66	9.05
Pyromucic	8.7	8.1	7.6	7.0
Benzoic	0.611	....	0.686	0.684
o-Toluic	1.59	1.49	1.37	1.25
m-Toluic	0.515	0.548	0.560	0.554
p-Toluic	0.383	0.410	0.433	0.437
o-Phthalic	13.4	....	12.6	12.2
Cinnamic	0.322	....	0.368	0.367
Salicylic	8.3	....	10.6	10.6
m-Hydroxybenzoic	0.725	....	0.798	0.789
p-Hydroxybenzoic	0.251	....	0.285	0 287
Gallic	0.338	....	0.385	0.394
Metanilic	0.90	1.33	1.99	2.62
Sulphanilic	3.28	....	6.55	8.18
o-Aminobenzoic	0.0306	....	0.0671	0.0824
p-Aminobenzoic	0.0448	....	0.0714	0.0790

The results obtained agree generally with those of Euler[1] and Schaller.[2] The former investigator, working at temperatures ranging from 0° to 50°, found that the dissociation of benzoic acid reached a maximum at 35°, while that of *m*-hydroxybenzoic attained a maximum between 25° and 35°. The dissociation of salicylic acid increased from 0° to 50°, while that of *o*-toluic acid decreased from 0°. Schaller, working at temperatures between 25° and 100°, found maxima in dissociation between 25° and 40° for cinnamic, benzoic, salicylic, *m*- and *p*-toluic acids, and observed, as the work of Euler and the results here recorded show, that the dissociation of *o*-toluic acid decreased with rise in temperature from the lowest temperature at which it was measured.

The hypothesis of Thomson[3] and Nernst,[4] which states that solvents having the greatest dissociating power have the largest dielectric constants, explains why the dissociation of inorganic salts and mineral acids decreases with rise in temperature, since it has been shown[5] that the dielectric constant of water decreases also with rise in temperature. Since maxima in dissociation have been found with many of the organic acids, other unknown forces must come into play in such cases. It is particularly interesting to note that such isomers as the toluic acids differ markedly with respect to the change of their dissociation with change in temperature.

SUMMARY OF FACTS ESTABLISHED.

1. The percentage temperature coefficients of conductivity of the organic acids are generally small and of the same order of magnitude, and decrease with rise in temperature and with increase in dilution. The coefficients expressed in conductivity units decrease with rise in temperature. These facts suggest that the acids are much less hydrated than the mineral acids, for reasons previously given.

2. The percentage coefficients of conductivity of the amino acids are exceptionally large, and the coefficients expressed

[1] Z. physik. Chem., **21**, 247 (1896).
[2] *Ibid.*, **25**, 497 (1898).
[3] Phil. Mag., **36**, 320 (1894).
[4] Z. physik. Chem., **13**, 531 (1894).
[5] Phil. Mag., [6] **7**, 655 (1904).

in conductivity units increase with rise in temperature. The internal salt-forming power of these amphoteric electrolytes explains such behavior.

3. The conductivity of most of the organic acids is a parabolic function of the temperature, as proved by comparing observed values with those calculated from interpolation formulae.

4. Several of the amino acids are again exceptions, and their conductivity is not a parabolic function of the temperature, for the same reasons which explain their large temperature coefficients.

5. There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between 25° and 35°, while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from 0°.

6. Isomeric acids do not behave similarly as regards change in their dissociation.

7. The migration velocities of isomeric ions are identical.

8. The behavior of the organic acids with respect to the change in their dissociation with the temperature is not in accord with the hypothesis of Thomson and Nernst, which connects dissociating power and dielectric constants; or at least the influence of some other unknown force is suggested.

This work will be extended for the organic acids from 35° to 65°, and also to nonaqueous solvents.

JOHNS HOPKINS UNIVERSITY,
June, 1910.

REVIEWS.

QUANTITATIVE CHEMICAL ANALYSIS. Adapted for Use in the Laboratories of Schools and Colleges. By FRANK CLOWES, D.Sc., Lond., Emeritus Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., Dublin, Head of the Chemical Department in the Southwestern Polytechnic, Chelsea, S. W. Eighth Edition. Philadelphia: P. Blakiston's Son & Co. 1909. pp. xxiv + 565. Price, $3.50.

The sixth edition of this well-known work has already been reviewed at some length in THIS JOURNAL.[1] In the present

[1] Vol. **31**, p. 299.

edition the type has been entirely reset, and considerable addition has been made to the text and illustrative cuts. The size of the page has been increased somewhat, while the thickness of the book remains about as before.

According to the authors, the new matter introduced is as follows: a description of improved water stills and steam ovens; additional methods for the determination of melting and boiling points, for the electrolytic estimation of metals, for the volumetric estimation of hydrogen peroxide, formaldehyde, silver, tin and antimony alloys, for the estimation of preservatives in milk and butter, resin acids in soap, and poisonous metals and dissolved oxygen in water; also additional processes for the valuation of the ores of chromium, tin, arsenic, mercury and zinc, of soap by a shortened scheme, of burnt lime, mortar, cement, white metal, and the description and use of the bomb calorimeter for coal valuation.

A new section has been introduced on the examination of oils, fats and waxes, and a table of the constants and characteristics of the ordinary members of this class of substances has been inserted by means of which the results of the examination may be interpreted.

The book is an excellent compilation of analytical methods and will, doubtless, prove very useful to both the chemist and the student; it is open to question, however, whether a total disregard of the modern theories of solution in quantitative analysis is justifiable from the standpoint of teaching.

E. B. SPEAR.

A MANUAL OF QUALITATIVE ANALYSIS. By J. E. MCGREGORY. Professor of Chemistry and Mineralogy in Colgate University. Revised Edition. Boston: Ginn & Co. 1909. pp. xiv + 135. Price, $1.00.

The first edition of this book, published in 1903, was reviewed in THIS JOURNAL.[1] The present edition is but little changed. It is thorough, carefully written and well arranged; it does not introduce modern theoretical or analytical methods. It may be recommended to the numerous teachers who prefer this type of book.

E. R.

AN INTRODUCTION TO CHEMICAL ANALYSIS, for Students of Medicine, Pharmacy, and Dentistry. By ELBERT W. ROCKWOOD, M.D., Professor of Chemistry and Toxicology and Head of the Department of Chemistry in the University of Iowa. Third Revised Edition. Philadelphia: P. Blakiston's Son & Co. 1909. Price, $1.50.

The first edition of the book appeared in 1902[2] and the second in 1905.[3] Although it contains only 240 pages, it em-

[1] Vol. **31**, p. 586.
[2] THIS JOURNAL, **27**, 235.
[3] *Ibid.*, **34**, 472.

braces qualitative analysis, volumetric analysis, the sanitary examination of water, the detection of poisons, analysis by the blowpipe, and the testing of reagents. Considerable attention is paid to the theory of electrolytic dissociation as a means of explaining the chemical reactions used in analytical chemistry, and this is, in the main, satisfactory, although the definition of solubility product is merely that it is "the product of the concentrations of the ions," and the fact that this is only true of a saturated solution is not made clear.

As a whole, the text is well written, although there is some evidence of careless statements. Thus the treatment recommended for insoluble tin oxide, and insoluble salts of lead and silver, is fusion with sodium carbonate on platinum. Again, in the detection of poisons, the author wisely points out the necessity of testing hydrochloric acid for arsenic, but forgets, in describing the test, that arsenic trichloride will distil off in concentrating a liter of acid to a volume of 20 cubic centimeters.

WILLIAM T. HALL.

FOOD INSPECTION AND ANALYSIS, for the Use of Public Analysts, Health Officers, Sanitary Chemists and Food Economists. By ALBERT E. LEACH, S.B., Chief of the Denver Food and Drug Inspection Laboratory, Bureau of Chemistry, U. S. Department of Agriculture. Second Edition, Revised and Enlarged. 40 full-page, half-tone plates. New York: Wiley and Sons; London: Chapman & Hall, Ltd. 1909. pp. xviii + 954. Price, $7.50.

The first edition of this work was published in 1904. But few American chemists were then giving special attention to the examination of foods. The Association of Official Agricultural Chemists had just published its first compilation of food methods, representing the beginning of the system of cooperation and collaboration among American food chemists which has characterized their more recent work. Material progress had already been made by the Association of Official Agricultural Chemists in determining proper standards of composition of foods, and the foundation had been laid for the broader subsequent work on the same subject by the committee appointed jointly by the Association of Official Agricultural Chemists and the Association of State and National Dairy and Food Departments.

The first edition of this work, therefore, was written early in the present period of activity and immediately took the first rank among books of its class. It is universally considered indispensable in every food laboratory.

The second edition is cast on the same lines as the first but is a complete revision and brought thoroughly up to date. Almost every page is materially altered. Many of

the methods of analysis given in the first edition and since found unreliable have been replaced by others. The new methods introduced cover a wide variety of subjects: "Notable among these are meats and meat extracts, flour (including methods for determining the grade and for the detection of bleaching), noodles and Italian pastes, paprika, prepared mustard, tea, coffee, cocoa products (including milk chocolate), ice cream, maple products, honey, oils (including the Polenske number and Bömer's phytosterol-acetate test for vegetable oils), distilled liquors, preservatives (notably benzoic acid), etc.

"A separate chapter on the refractometer, its varieties and application to food analysis has been introduced; also a separate chapter on flavoring extracts, including the lesser used extracts of almond, peppermint, wintergreen, rose, cassia, and cloves."

In its second edition, the book is brought up to date and in many portions—notably in Chapters 10, 13, 14 and 15—it has been greatly strengthened. The preface gives to Dr. A. L. Winton credit for the greater portion of the work of revision, as the author was not at that time able to undertake it alone. It brings to us, therefore, the judgment and experience of two of the foremost food chemists.

The book is peculiarly a laboratory manual and is intended for the analyst alone. The work of the inspector is discussed only with reference to his relation to the analyst, while the subject of the prosecution of court cases is dismissed with a brief discussion of the testimony of analysts and with the statement that Massachusetts has found legal counsel superfluous in the trial of food cases in the lower courts.

It is the belief of the reviewer that the last statement is not applicable to the enforcement of the federal law or the laws of the majority of the states, especially in the trial of wealthy defendants who are represented by able counsel.

W. D. BIGELOW.

CHIMICA GENERALE E APPLICATA ALL'INDUSTRIA. Vol. II. Chimica Organica. DR. ETTORE MOLINARI. Milano: Ulrico Hoepli. 1908. pp. 980.

The multiplication of comprehensive and standard works on special branches of chemistry in all languages is a notable sign of the flourishing condition of this science. The present work in Italian is fully comparable with the best works on chemical technology such as we usually owe to the thoroughness of German chemists and the enterprise of German publishers. It is in no sense an imitation of one of these but

combines originality of subject matter with an excellent summary of organic chemistry as applied to the arts. The theoretical part, while necessarily brief, is clear and well compiled; a good feature is the number of tables of physical properties of homologues and isomers. As an illustration of the inclusive character of the technical portion may be cited articles on theories of the origin of petroleum, oxydases, alcoholism and its sociological influence, velocity of propagation of explosions, safe explosives for dangerous mines, destruction of explosives, saponification of fats by biological means (lipolytic enzymes), synthesis of alkaloids, artificial silk, etc. The book is to be highly recommended to those who read Italian.

B. B. TURNER.

BEET-SUGAR MAKING AND ITS CHEMICAL CONTROL. By Y. NIKAIDO. Easton, Pa.: The Chemical Publishing Co.

To quote from the preface: "The aim of this work is to aid those who are starting their career in the beet-sugar manufacture but lack systematic training in the technique thereof. Having this in view, the author has endeavored to explain not only the practical operations of sugarhouse stations but also the fundamental principles involved in the various processes of the sugarhouse and in the methods of analysis of various sugarhouse products."

In his endeavor to accomplish his purpose as outlined above, the author has condensed, in some two hundred and ninety odd pages, text covering the chemistry of the industry, inorganic and technical, as well as detailing processes and analytical methods and discussing the optics of the polariscope. The book shows much painstaking compilation and the subject matter is logically arranged, but aside from directions for analytical methods and description of processes and apparatus with which the author shows familiarity, the text is little more than a collection of notes such as any bright student might elaborate from his lecture courses. Great condensation is of course necessary for covering such an extensive field and that the quality of the text would be somewhat uneven is also obvious.

To the young chemist entering on his industrial career, who, as a rule, is continually looking for the book which will tell him all things necessary to know, Mr. Nikaido's work will be attractive, and perhaps even if the novice fails in getting a working knowledge of much that is presented, the book may prove the inspiration needed for more extended study. To the experienced man the book will be useful for handy reference.

The descriptions of apparatus and manipulation directions are clear and aided by numerous illustrations, although there is practically nothing on that useful and often abused instrument, the balance.

A commendable feature of the book is Table IV, an elaborate work arranged in an original manner, and comprising thirty-six pages of the appendix, which gives values for sucrose and purity for all sugarhouse liquors between 7°.1 and 27° Brix for each tenth. By an ingenious adaptation of Weisberg's dilution method, the same table can be used for massecuites and molasses. It should be stated, however, that such tables, although used in one form or another almost universally in refinery practice, are only correct when polarizations are made at the standard Brix temperature. An analysis of the formula on which such tables are collected will show that the density should always be taken at *temperature of polarization* for calculating sucrose, the Brix reading, of course, being calculated for standard temperature. (The reviewer confesses that he has not been clear on this point in his own book, by the way.) The error at maximum room temperatures is but a few tenths of a per cent. and can be shown experimentally by comparing results with those obtained by using an accurate sucrose pipette or by polarizing the normal weight of solution. Hence it is negligible when the table is used for comparative purity work, but should be taken into consideration in determining the sucrose content of juices and other liquors. Used understandingly, this table of Mr. Nikaido will prove most useful to all sugar chemists.

GEO. W. ROLFE.

THE ELEMENTS OF METALLOGRAPHY. By DR. RUDOLPH RUER. Privatdozent at the University of Göttingen. Authorized Translation by DR. C. H. MATHEWSON, Instructor in Chemistry and Metallography at the Sheffield Scientific School. New York: John Wiley & Sons. 1909. pp. xvi + 342. Price, $3.

This volume represents a very desirable addition to the rather few text-books on metallography. The book is divided into two parts, the first of which is devoted to a discussion of the thermal equilibrium diagrams for one-, two- and three-component systems, most attention being paid to the binary alloys. Methods, other than thermal, for the investigation of equilibrium curves and for solidified mixtures are given in the supplement, and the discussion of the phase rule is also reserved for supplementary treatment. The explanations of the various types are given in great detail and the criteria for distinguishing the various constituents of an alloy, such as eutectic, compound, etc., are especially commendable.

The second part is devoted to the practice of metallography and deals with the thermal and structural investigation of alloys. A collection of references to about two hundred and seventy-five binary fusion diagrams of metallic alloys is given at the end of the book.

In spite of the general excellence of the work, there are some errors of translation which are liable to prove exceedingly confusing to the beginner, the portion dealing with the iron-carbon diagram being especially misleading. Thus by incorrectly translating "zurückgegangen" as "prominent", the translator would have the reader believe "that the tendency toward formation of incompletely stable crystalline varieties (cementite!) becomes very prominent in the case of alloys of appreciably higher carbon content than corresponds to B′ (4.2 per cent. C)" and that this causes uncertainty as to the position of the curve representing primary separation of cementite from the melt. Such uncertainty is really caused not by the tendency of cementite to separate but from the prominent tendency of graphite to separate when the carbon content exceeds the above value.

Throughout this section "Temperkohle" is wrongly translated as "hardening carbon" instead of as "graphitic temper carbon."

The reviewer would scarcely agree with the translator that tempering effects a partial separation of cementite into ferrite and graphite, although annealing of high-carbon steels tends to produce this result.

In the preface the author states that the phase rule is reserved for the supplement on account of a disinclination on the part of the beginner to use it. In the reviewer's opinion there are other equally good reasons wherefore the student of metallography should early overcome such disinclination, first because the phase rule is undoubtedly the most easily applied and most general criterion as to the validity of any proposed system, and secondly, it is of almost universal occurrence in the literature dealing with heterogeneous equilibrium, especially as applied to alloys. H. E. K. R.

THEORIEN DER CHEMIE. Nach Vorlesungen gehalten an der Universität von Kalifornien zu Berkeley. Von SVANTE ARRHENIUS. Mit Unterstützung des Verfassers aus dem englischen Manuskript übersetzt von ALEXIS FINKELSTEIN. Zweite, neubearbeitete und bedeut vermehrte Auflage. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1909. pp. ix + 169.

The appearance of the first edition of this book has already been noticed in THIS JOURNAL.

The changes, and especially additions, that have been

made to the second edition can be best gathered from the author's own statement:

"Die rastlose experimentelle Arbeit, welche unsere Zeit auszeichnet, hat inzwischen sehr viel Material zu Tage gefördert, welches ich im Interesse des Lesers in dieser zweiten Auflage berücksichtigt habe. Besonders gilt dies für das Gebiet der Radioaktivität, welches für die theoretische Chemie von der grössten Bedeutung ist, da es einen Einblick in die Zusammensetzung der Atome gewährt. Auch die atomistische Auffassung der Materie ist durch die Forschung auf diesem und anderen Gebieten stark befestigt worden. Die Lehren von der Reaktionsgeschwindigkeit und von dem chemischen Gleichgewicht haben ebenfalls bedeutend an Umfang gewonnen und speziell auf dem wichtigen physiologisch-chemischen Gebiete grosse Landgewinne gemacht, die nicht ganz vernachlässigt werden konnten. Viele von den offenen Fragen sind durch eingehende Prüfungen, besonders von P. Walden, beleuchtet und teilweise erledigt worden. Alle diese Umstände führten dazu, dass die neue Auflage bedeutend umfassender geworden ist, als die erste." H. C. J.

RECENT ADVANCES IN PHYSICAL AND INORGANIC CHEMISTRY. By A. W. STEWART, D.Sc., Lecturer on organic chemistry in the University of Belfast. Formerly 1851 Exhibition Research Scholar and Carnegie Research Fellow. With an Introduction by SIR WILLIAM RAMSAY, K. C. B., F. R. S. London, New York, Bombay and Calcutta: Longmans, Green & Co., 1909. pp. xiv + 267. Price, $2.50.

The book is, as the author states, about equally divided between inorganic and physical chemistry, as the contents will show: Some hydroxylamine derivatives; Colloids; Reactions in liquid ammonia; The fixation of nitrogen; Double salts; The problem of the oceanic salt deposits; The cobaltamines; Absorption spectra; The elements of the rare earths; Atomic weights; The inactive gases; The radioactive elements; Radioactive changes; Radioactive emanations.

In the two introductory pages by Ramsay several important matters are referred to. Ramsay likens Dr. Stewart "to a skilful cook who has trimmed his joint, rejecting all innutritious and redundant excrescences and has served it up to table in a palatable form. Such essays, I venture to think, will do more to encourage a taste for chemistry than many text-books."

Says Ramsay: "This book, it may be hoped, will have a still further use; it cannot be doubted that some who peruse it will have suggested to them various directions in which they may profitably attempt to increase knowledge. Nothing is

so sad as to see much time and labor spent, with patience and devotion, in the investigation of some matter which possesses no real importance. It may be retorted that every true statement is of importance, but this is not so. It is only statements which hold forth some prospect of contributing to an organic whole which can be held valuable. There may, perhaps, be a little more merit in ascertaining to the hundredth of a degree the boiling point of sulphur than of measuring the area of the wings of some particular butterfly; but the difference is barely appreciable. One is as likely to prove useless as the other. It would be well if enthusiasts anxious to carry on research would remember that it is much more stimulating to carry on an interesting than an uninteresting research. It is, I believe, not improbable that the reading of such a work as this may aid those imbued with the spirit of investigation to make a happy choice of a subject of research. Should this hope be realized, Dr. Stewart will have done a most useful work."

The book seems to be very well written and treats of the chosen chapters in an interesting way, but one notes the absence of a large number of subjects of fundamental importance for physical chemistry. Indeed, some of the subjects omitted seem to be of far more importance than some that are included in this work. However this may be, the book will doubtless serve a useful purpose. H. C. J.

ÜBER DIE ERHALTUNG DER MASSE BEI CHEMISCHEN UMSETZUNGEN. Von H. LANDOLT. Abhandlungen der Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie. Herausgegeben im Auftrage der Gesellschaft von PROF. DR. R. ABEGG, in Breslau. Halle a/S: Verlag von Wilhelm Knapp. 1909. pp. viii + 47. Price, M. 1.80.

The results of this classical investigation of Landolt, on the question of whether there is a change in weight when chemical reaction takes place, are brought together in a very convenient form in this little monograph. This investigation, extending over seventeen years, is to be ranked among the most refined that have ever been carried out in chemistry, or in any other branch of science. The finest balances were used and the greatest care taken at every step in the work.

The conclusion drawn by Landolt from all of his work is as follows: "The final result of the entire work is that in the 15 chemical reactions studied, no change in weight could be shown to have taken place."

This work should be carefully studied by all who contemplate carrying on scientific research. H. C. J.

BEITRAGE ZUR KENNTNIS DES ELEKTROCHEMISCHEN VERHALTENS DES EISENS. Von F. FOERSTER. Aus dem Laboratorium für Elektrochemie und physikalische Chemie an der Technischen Hochschule zu Dresden. Halle a/S: Verlag von Wilhelm Knapp. 1909. pp. 83. Price, M. 3.20.

This pamphlet is one of the Abhandlungen der deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie. The larger divisions are: The electromotive force of iron; The electrolytic separation of iron; and Electrolytic iron.

Some of the more interesting subdivisions are active iron, discussing also the condition of the "passive state;" active iron and the amount of hydrogen contained in it; iron rendering itself active; iron rendered active by the halogens; and the hydrogen content of electrolytic iron.

The section dealing with the "passive state" of iron is one of the most important in this monograph. The two theories of passivity that have attracted the greatest attention are: first, that the passive metal is covered with a layer of oxide, a view which is now scarcely tenable, and the reaction velocity theory, which says that ions of low valence dissolve slowly. The author thinks that the presence of hydrogen in iron and correlated elements has much to do with rendering these metals active.

The subjects dealt with are discussed in a clear, and, for the most part, attractive style. H. C. J.